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THE INFLUENCE OF TEMPERATURE ON THE PHOTOELECTRIC EFFECT OF THE ALKALI METALS

By Herbert E. Ives and A. L. Johnsrud

ABSTRACT

Special cells having a hollow central cathode were immersed in liquid air for an extended period to insure that any gases, if present, were condensed on the outer alkali metal coated walls. The temperature of the cathode was controlled by a stream of evaporating liquid air, whereby all temperatures between +20 and −180°C could be attained and held constant and be measured. In these cells the variation of photoelectric current with temperature in sodium, potassium, and rubidium is continuous, without abrupt changes. The effect is relatively small for sodium, showing hardly at all for blue light or white light, but clearly for yellow light. The behavior of rubidium is similar to that previously reported for potassium.

In a second form of cell, potassium was collected in a deep pool. By slowly cooling the metal from the molten condition, smooth crystalline surfaces were obtained. With these annealed potassium surfaces, the variation of photoelectric current with temperature is represented by curves varying systemmatically in shape with the color of the light, and the effect is far greater than previously reported, amounting, for yellow light, to a variation of 10 to 15 times between room and liquid air temperature. When the surface is roughened curves of the previously reported type are obtained. Small pools give erratic effects, showing changes in opposite directions for different portions of the temperature range. It is concluded that the variation of photoelectric effect is intimately connected with the strains produced in the surface by expansion and contraction with temperature.

INTRODUCTION

The experiments here described were undertaken for the purpose of extending the work reported by one of the present authors on the influence of temperature on the photoelectric effect in potassium.[1] The specific objects for which the new work was undertaken were two: (1) to extend the work to other alkali metals than potassium. (2) to follow the variation point by point through the whole temperature range of which only the extreme points, namely room temperature and liquid air temperature, were fully studied in previous work. Develop-

[1] Ives, J.O.S.A. & R.S.I., p. 551, April, 1924.

ments during the progress of the work, and the publication of results by other investigators induced us to broaden the originally planned scope of the work, so as to include a study of the influence of the character of the photoelectric surface upon the results.

EXPERIMENTS ON SODIUM, POTASSIUM, AND RUBIDIUM SURFACES OBTAINED BY CONDENSATION

The first series of experiments to be described were made with cells of a type similar to one used in the previous investigation (Fig. 1). In this, the alkali metal is condensed on the outer surface of a hollow cylindrical enclosure A at the center of the cell, and also upon the walls of the cell. As in the previous work, the cell is placed in liquid air for a long period before observations begin, on the assumption that if any gases or vapors are present which are condensable by the alkali metal at the lowest temperature used, they would thereby be condensed on the walls of the cell. (The usual charcoal tube shown at 13, was, in these experiments kept immersed in liquid air from the time the cell was taken off the pump until the conclusion of all measurements.) The smaller inner hollow electrode is then maintained at the various temperatures, and observations of the photoelectric current from it to the other electrode, are made. Illumination is through a diagonally attached side tube, with opaque walls, whereby the necessity for passing the light through a layer of liquid air, as in the earlier cells, is avoided. In order to obtain any desired temperature, the liquid air evaporation system, also shown in Fig. 1, was employed. This resembles in its general scheme one used by Cioffi and Taylor.[2] The cold air as evaporated from the liquid state in a side vessel F is carried to the lower end of the inner cylindrical electrode by means of a double-walled pyrex tube and ejected into a pile of glass beads B through which it discharges to the outer air. The temperature of the bulb and hence of the metal surface thus depends on the rate of evaporation of liquid air in F, which is controlled by the current through the heater coil C. In order to measure this temperature a platinum-constantan thermocouple was used.

It is, of course, essential for the validity of the results that the temperature over all parts of the illuminated electrode be the same. In order to test this point a special thermocouple was inserted with its two junctions lying one at the top and one at the bottom of the portion of the electrode coated with the alkali metal. Any difference in tem-

[2] Cioffi and Taylor., J.O.S.A.&R.S.I., *6*, p. 906; 1922.

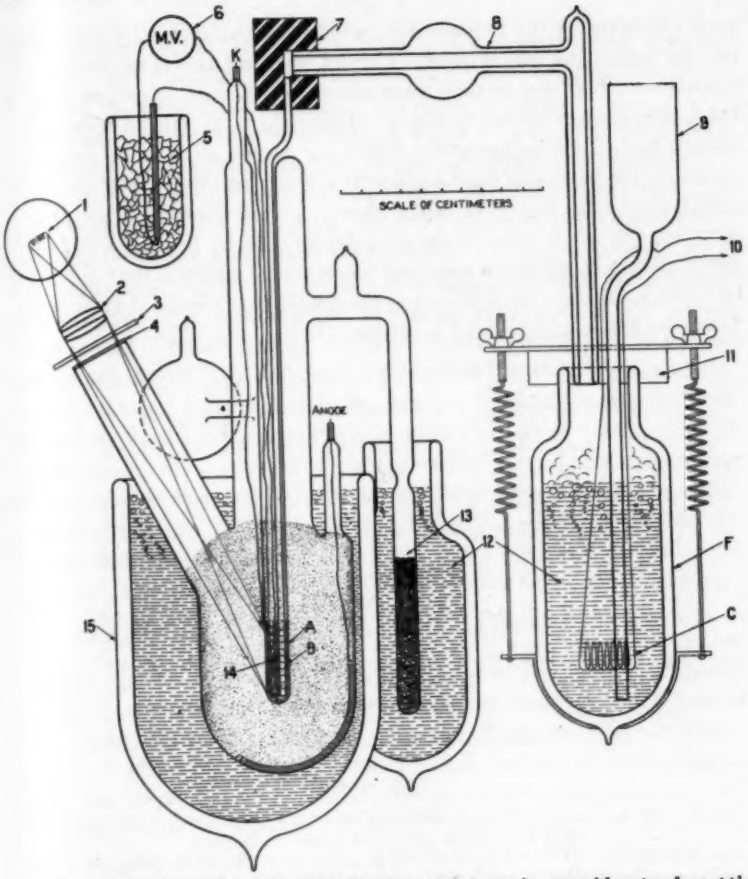

FIG. 1. *Section of photoelectric cell used in first series of experiments, with system for supplying evaporating liquid air to hollow central electrode.*

1. *Lamp used as source of light.*
2. *Lens.*
3. *Color filter.*
4. *Quartz window.*
5. *Ice in Dewar flask for one junction of thermocouple.*
6. *Millivoltmeter for temperature readings.*
7. *Rubber serving as elbow for cold air stream.*
8. *Double-walled pyrex tube with space between walls exhausted and silvered.*
9. *Pyrex funnel*
10. *Battery leads for heater current.*
11. *Fitted cork cover surrounded by brass ring.*
12. *Liquid air.*
13. *Charcoal tube.*
14. *Junction of platinum-constantan thermocouple measuring temperature.*
15. *Large pyrex Dewar flask.*

perature between the two portions would thus be shown by deflections on the indicating instrument. Curves showing the temperature difference as a function of time after the change of rate of evaporation of the liquid air are shown in Fig. 2. From these, it will be seen that a steady flow of the evaporating liquid air causes, as is to be expected, an initial inequality of temperature at the top and bottom of the alkali metal electrode, but that when this flow has continued for 3 to 5 minutes, the whole mass of the glass beads, and by inference the alkali metal electrode, attains a constant temperature which is that measured by a single thermocouple placed at the center of the mass of glass beads. Temperatures could be read to within 1.0°.

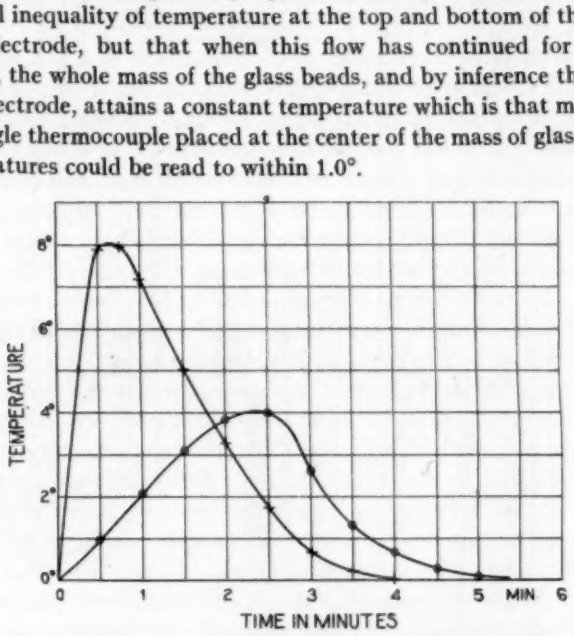

FIG. 2. *Temperature difference between top and bottom of central electrode as function of time after changing the rate of evaporation of liquid air.*

The results of the experiments made with this apparatus on sodium, potassium, and rubidium cells are shown in Fig. 3. One set of symbols, as shown by the annexed key, represents series of data taken when the temperature was increased between consecutive readings, the other set represents data obtained with decreasing temperatures. It is obvious that there is no trace of a hysteresis effect.

With regard to the specific problem under study, the dependence of photoelectric current upon temperature, the results for potassium are found to agree with those previously described. The photoelectric current decreases with decreasing temperature, the effect being greater for yellow than for blue light. With rubidium, similar results are obtained; the variation for both yellow and blue light being less than that

found for potassium. This may, in part, be due to the fact that the threshold wave length of rubidium is more remote from the wave lengths of the irradiating light than is that of potassium.

The results for sodium are of special interest. Hurt[3] has announced experiments with sodium which showed no change of photoelectric current in the interval from zero to $-180°$. It will be seen from the results shown in Fig. 3, that with blue light and with white light, which is effectively largely blue, there is practically no change between room temperature and $-180°$. When, however, sufficiently long wave length energy is used, e.g., yellow light, the same depression of the photoelectric effect is found as with the other two alkali metals. Attention may be called to a new phenomenon appearing with sodium, namely, an increase of the photoelectric current for blue and white light for the intermediate temperatures in the neighborhood of $-80°$. This, it may be remarked, cannot be explained on the ground of a simple continuous increase of the work function of the surface such as was found in the previous investigation to be a satisfactory explanation of the phenomenon found with potassium. The occurrence of a similar effect with a rough potassium surface will be described later in the paper.

EXPERIMENTS WITH ANNEALED ALKALI METAL SURFACES

During the progress of the experiments just described Hornbeck,[4] working on the same subject, confirmed the existence of a considerable temperature effect for potassium. Working, however, with an experimental arrangement designed to permit observations at any temperature in the whole range in question, he apparently found a sharp discontinuity in the photoelectric current at approximately $-80°$. From this he suggests that the variation in photoelectric effect with temperature is associated with a change in crystal structure at this temperature, which is indicated from phenomena of entirely different character.[5]

In view of the fact that we found no sign of a discontinuity we studied Mr. Hornbeck's results in order to find if possible a reason for this discrepancy. We believe there is some cause for doubt as to the reliability of Mr. Hornbeck's temperature measurements, as he himself suggests. At the same time it is very difficult to explain the very definite character of his curves by supposing the temperature of his photoelectric cell enclosure to be non-uniform. In considering all the differences between

[3] Hurt, Phys. Rev., p. 207, Aug., 1924.
[4] Hornbeck, Phys. Rev., p. 631, Dec., 1924.
[5] Bidwell, Phys. Rev., p. 357, Oct., 1924.

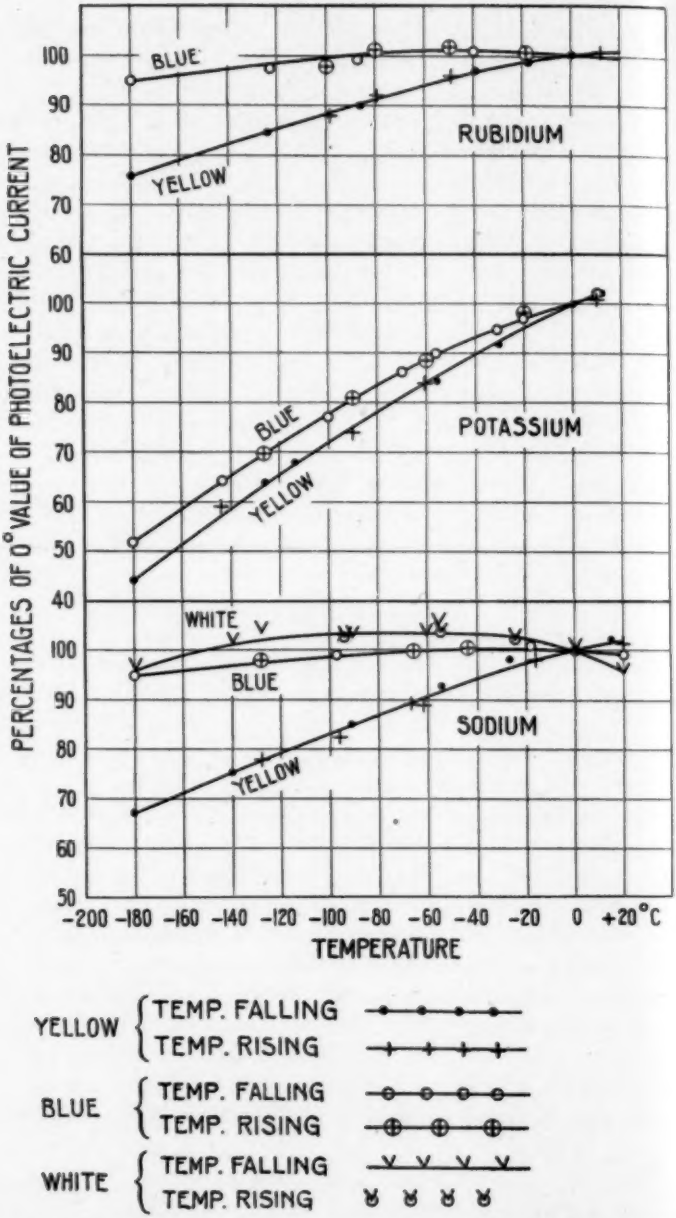

FIG. 3. *Effect of temperature on photoelectric currents from sodium, potassium, and rubidium.*

his experiments and ours, we noted one condition which was definitely different, and that is the *surface* of the alkali metal in two cases. In our experiments the alkali metal exists in the form of fine globules and rough areas as obtained by condensation on a cool surface. In Mr. Hornbeck's cell the alkali metal was in the form of a large pool which he states showed a *specular* surface. Thinking that this difference in form and surface might effect the results, we have made further experiments, to be described below, in which we have endeavored to secure specular surfaces of alkali metal, and at the same time preserve the reliable temperature control used in the work just described.

In the course of extensive earlier work we had ascertained that under certain conditions it was possible to secure fairly smooth potassium surfaces showing flat crystalline areas of highly specular character. The necessary condition appears to be the very slow undisturbed cooling of the surface. We accordingly prepared several cells of the design shown in Fig. 4. In these cells, the alkali metal is in the form of a frozen pool at the bottom. The anode consists of a metal ring from which a stiff wire is carried up through the long stem shown. This type of cell is undesirable from many standpoints, among which may be mentioned the opportunity for accumulating static charges on the walls. It has, however, appeared necessary to compromise with certain requirements in order to obtain a form which could be handled with the temperature control apparatus. For this purpose, the later apparatus was modified to the extent of placing the whole cell in a Dewar flask in which glass wool was lightly packed, and discharging the stream of cold air against the cell from a series of orifices through the inside wall of a circular tube, T. The temperature of the potassium was measured by a thermojunction touching the bottom of the cell, and a differential thermocouple, shown in the figure, was used to determine the interval between changing the rate of evaporation of the air and making the observations necessary to ensure uniformity of temperature. The whole outside of the cell was painted black with asphaltum varnish with the exception of an aperture in the top bulb through which the light entered. Observations were in general made with several colors of light as obtained through color filters placed in a frame so that the effects of all colors could be observed successively at any one temperature.

In order to secure the specular, or more properly the crystalline surface desired, the cell was placed on an antivibration suspension and immersed in a Dewar flask filled with oil at a temperature somewhat above the melting point of the alkali metal. This was then allowed to

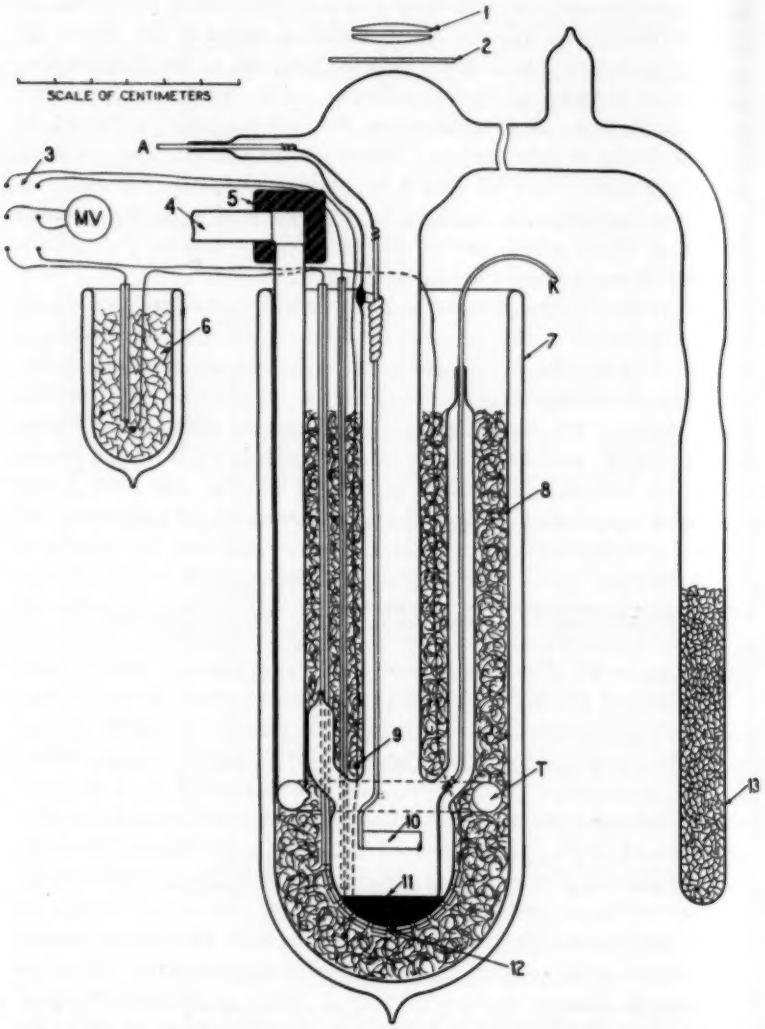

FIG. 4. *Second form of photoelectric cell with its temperature controlling and measuring apparatus.*

1. *Lens.*
2. *Color filter.*
3. *Switch.*
4. *Tube for influx of cold air.*
5. *Rubber serving as elbow for cold air stream.*
6. *Ice in Dewar flask for one junction of thermocouple.*
7. *Dewar flask.*
8. *Glass wool.*
9. *One junction of differential thermocouple.*
10. *Nickel ring anode.*
11. *Pool of metal.*
12. *Junction of platinum-constantan thermocouple.*
13. *Charcoal tube*

cool down spontaneously until it attained room temperature, which was a matter of a number of hours. The surfaces obtained with potassium in this manner, show a uniformity of appearance over the whole surface and a highly specular character which are very satisfactory. Equally good surfaces of the other alkali metals could not be obtained;

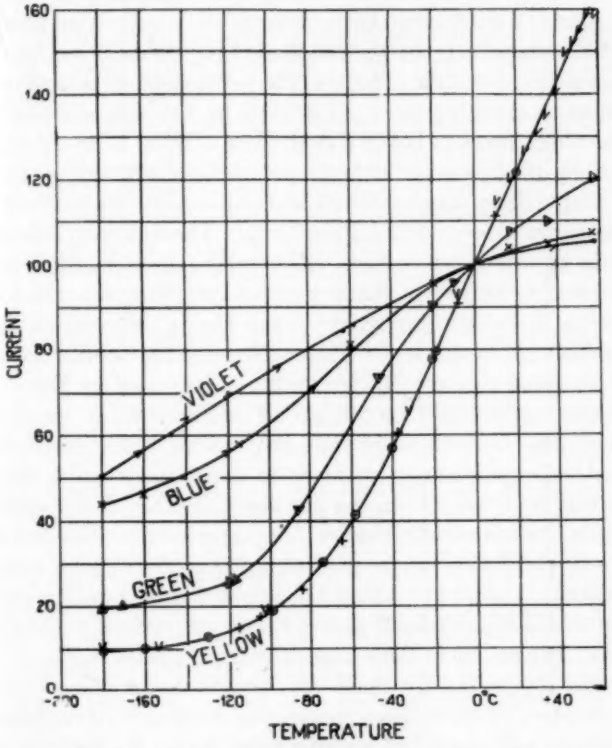

FIG. 5. *Variation of photoelectric effect with temperature in annealed specular potassium surface.*

these exhibited ridges, as well as irregularities in the shape of the meniscus, which made it seem doubtful a priori whether homogeneous surfaces could be produced. In conformity with these observations, the results obtained with the potassium surfaces were much more uniform and apparently significant than with the other metals.

A set of curves obtained with a potassium cell prepared in this way is shown in Fig. 5, where the curves for various colors have been plotted

to equal values at 0°C. Where two sets of symbols are used on one curve they indicate rising and falling temperatures respectively. It will be noted that the decrease of photoelectric effect with temperature is not only present but is exhibited to far greater degree than has been previously noted. For yellow light a change from a temperature slightly below the melting point to the temperature of liquid air is represented in the photoelectric current by a factor of 16 to one. With green, blue, and violet, the effects are progressively less. In addition, the curves differ in shape, for while the curve for yellow light is throughout concave upward, there is a point of inflection in the green and blue curves, and the violet curve is concave downward. There is no hysteresis, as is shown by the agreement between points taken with rising and points taken with falling temperatures; and the curves are entirely reproducible, as was proved by additional runs. These curves, although obtained in an attempt to imitate Hornbeck's conditions, bear no great resemblance to his except that a point of inflection occurs in his as in ours, with downward concavity in the higher temperature and upward concavity in the lower temperature segment of the curve. It should be noted that the different wave lengths used by Hornbeck all lie so close together that they might all be described as "green light."

The contrast between these and our previous curves was so striking that further experiments were made to determine whether they were in fact due to differences in the physical condition of the potassium, in those as contrasted with our previous experiments. The first experiment to be performed was to produce deliberately a rough matte surface on the potassium by cooling it suddenly from the molten condition and also distilling additional potassium on the surface, while this was still cold. The results of these experiments are shown in Fig. 6. These curves are approximately those obtained with the thin rough condensed surfaces of the earlier experiments, showing less variation with temperature, and much less striking curvatures. As the next experiment, the potassium was once more melted and put through the annealing process. Measurements made on the cell with yellow light after this operation are shown in Fig. 7, in which it will be seen that while relative changes due to temperature are somewhat altered, the general character of the curve originally obtained with the specular surface is again reproduced. An additional experiment intended to test the same question was performed on another cell. In this the potassium was first introduced as a thin layer, formed by distillation on the walls of the cooled bulb; and an additional supply of metal was held in reserve in

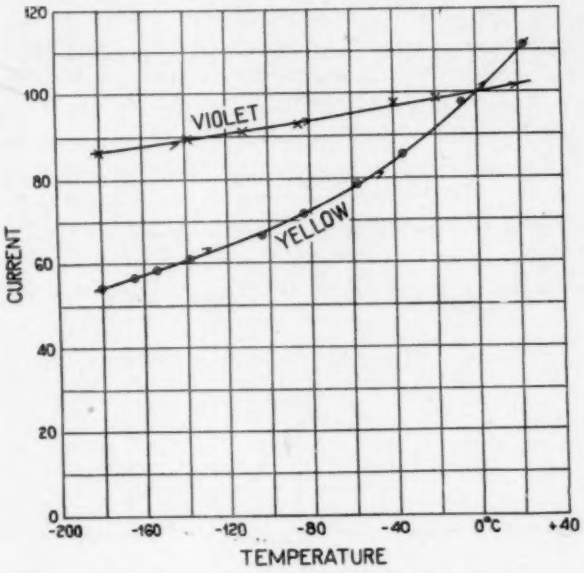

FIG. 6. *Same cell as Fig. 5 with surface roughened.*

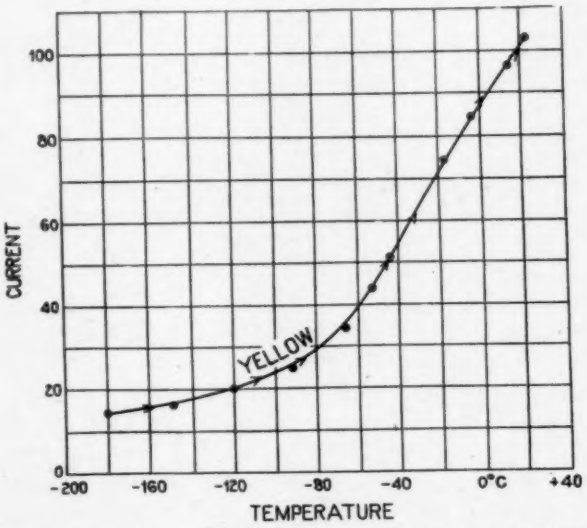

FIG. 7. *Check curve for yellow light, on same cell as Figs. 5 and 6, after re-annealing.*

a side bulb. The cell in this condition when carried through the temperature range, yielded the measurements shown in the curves of Fig. 8. These curves are in every essential respect similar to those found with the earlier types of cells, in which the alkali metal was in the form of a thin rough layer obtained by distillation. It will be noted that the curve for blue light shows the same type of maximum at intermediate temperature as that found in sodium in the first series of measurements described in this paper. Following these measurements a portion of the potassium in the side tube was melted and caused to flow into the main bulb, until this was about half full. The pool thus formed was

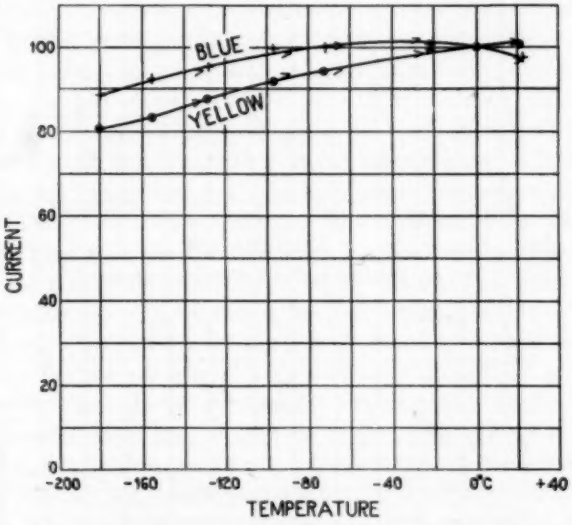

FIG. 8. *Photoelectric effect versus temperature curves for thin condensed film on interior of bulb of cell of type shown in Fig. 4.*

then put through the annealing process already described, and remeasured. Fig. 9 shows the results found. They agree in essentials with those obtained with the first cell of this type.

A group of several cells of this design were made up. Of these, the majority showed the behavior exhibited in Figs. 5 and 9. Other cells behaved somewhat differently. In one, the photoelectric current showed a slight rise at the lowest temperatures. Another showed a rise at first as the temperature was lowered, followed by a fall; and in this cell (Fig. 10) the rising and falling temperature curves did not follow the same course. Examination of these cells, and additional experiments

on other cells, support the generalization that if the potassium pool has a large, plane, specular area, and is so large that the amount of light falling on the free surface greatly exceeds the amount of light falling near its edges, the regular curves of the type of Fig. 5 are uniformly and easily obtained. If, however, the pool is quite small, so that a considerable part of the light falls on its edges, or again if the wall of the bulb is rough or dirty, so that the potassium does not flow easily over

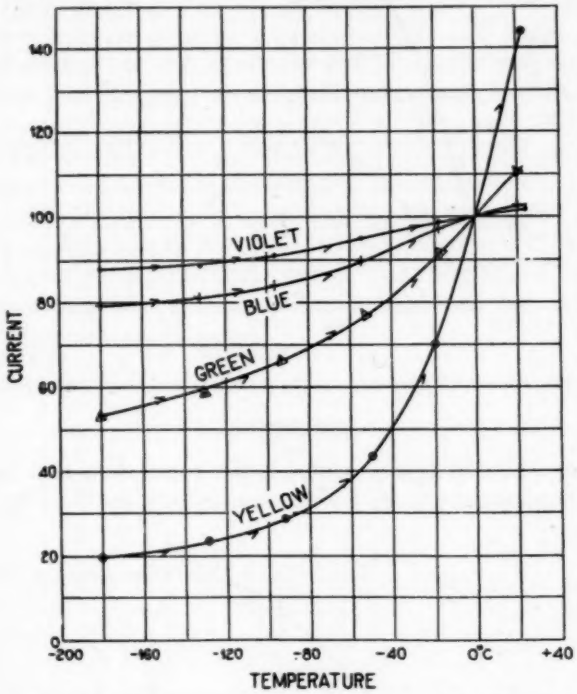

FIG. 9. *Photoelectric effect versus temperature curves for annealed solid pool of potassium formed in same cell as thin layer whose measurements are given in Fig. 8.*

it when liquid, (clean potassium wets the glass, forming a concave meniscus) distorted and erratic current-temperature curves are obtained.

Attempts to produce the crystalline specular surfaces obtained with potassium, with the other alkali metals, have not thus far been successful. They exhibit the erratic non-reproducible type of current-temperature curve associated in potassium with small area pools, and have not

as yet been fully studied. It may be remarked that the overall change with caesium, when the temperature is dropped from +20°C to −180°C is very great.

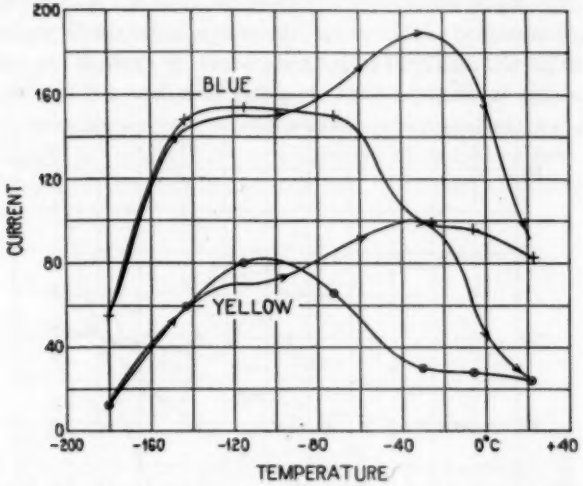

FIG. 10. *Photoelectric effect versus temperature curves for very small pool of potassium.*

DISCUSSION

The experimental data presented in this paper show that the variation of the photoelectric effect of the alkali metals, produced by varying

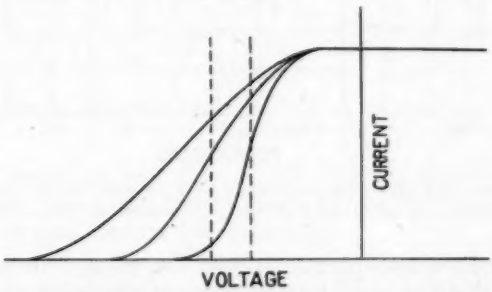

FIG. 11. *Suggested explanation of temperature effect as shift of work function value.*

temperature, is generally in the same sense as the variation of the temperature. The only apparent exceptions occur when the metal surface is restricted and the walls of the tube rough and contaminated, and are perhaps to be ascribed to local tensions resulting from the freezing of

the metal while adhering to the glass. Large smooth surfaces of potassium display so enormous a variation of photoelectric effect with temperature as to suggest that they alone reveal the true behavior of potassium, which with rough surfaces is partly concealed by secondary agencies.

It may be pointed out that the curves of Fig. 5 are of the form which would be obtained by a shift of the work function provided the effect of the work function on the distribution of energies among the photoelectrons is as shown in Fig. 11. Here the voltage-current curves for all colors of light are assumed to be of similar flat "S" shape, starting from the same upper limit of voltage and differing in extension along the voltage axis. The vertical lines mark various work functions, measured from the common saturation point of all the curves. On the views embodied in this figure the photoelectrons possess a certain distribution according to energies, inside the metal. A definite amount of energy is subtracted from each electron on passing through the surface. All electrons possessing energies less than the work function fail to emerge, those possessing greater energies emerge, their distribution according to energy *when referred to the interior of the metal* remaining unchanged.

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Analysis of Band spectra ascribed to PbH.—It was discovered by Grebe and Konen that the band in the spectrum of lead at 4270A is displaced by about .055A toward shorter waves when uranium lead, of combining weight 206.0, is used instead of ordinary lead, of combining 207.2 (a value which is itself a weighted mean for a mixture of isotopes). This displacement agrees very well with the value calculated from the assumption that this is a rotation-plus-oscillation band of a molecule of Pb; while the lines constituting the band are much sharper in the former case than in the latter, as should result from the fact that the former material is a single isotope, the latter a mixture of several. From the spacing of the lines in the band it follows that the molecule has moment of inertia amounting to $8 \cdot 10^{-40}$, which if it is PbH corresponds to a distance 2.2A between nuclei, which is plausible.—[E. S. Bieler, MacGill; Nature, *115*, p. 980; 1925].

KARL K. DARROW

Absorption of Mercury Vapor by thin Films of alkali Metal.—If a gram of sodium or potassium, enclosed in a tube evacuated except for mercury vapor, is distilled so as to cover a few cm^2 of the wall of the tube, the pressure of Hg vapor sinks to as low a value as though the tube were connected with a liquid air trap—to a value of 5.10^{-9} mm in one cited case with potassium, even this feeble pressure being supposed partly due to residual vapors of other sorts. The mercury remains securely entrapped for weeks, and the potassium film has been observed to absorb 150 per cent of its own weight of mercury. "The passage of several liters of moderately dry air at atmospheric pressure over the potassium has no serious effect on its power to trap mercury vapor," although the surface becomes discolored.—[A. L. Hughes and F. E. Poindexter, Washington University; Nature, *115*, p. 979; 1925].

KARL K. DARROW

Magnetic and non-magnetic Sesquioxides of Iron.—Given Fe_3O_4 in the form of a black powder to start with, it may be oxidized by direct ignition in air into a red sesquioxide which is not magnetic, or by heating at 200° to 250° in a current of air into a brown sesquioxide which is "violently ferromagnetic with a magnetism near that of magnetite." Transformation of the latter form into the former occurs at temperatures of 650° and higher.—[H. Abraham and R. Planiol, C.R., *180*, pp. 1328-1329; 1925.]

KARL K. DARROW

GENERALIZATIONS OF THE RAYLEIGH FORMULA FOR MOLECULAR SCATTERING

By John Q. Stewart

ABSTRACT

A unified treatment of the Rayleigh, Einstein-Smoluchowski, and Cabannes-King formulas.—Schuster has shown that the well-known Rayleigh formula for molecular scattering of light can be derived from general wave theory without special postulates (customarily introduced) which are peculiar to the elastic-solid, the electromagnetic, or the electron theory. The present report—the content of which is theoretical and mathematical—discusses the restrictions of the Rayleigh formula; and extends Schuster's demonstration to the two generalizations which have been developed, respectively, by Smoluchowski and Einstein, and by Cabannes and King. The former applies to dense media, and the latter to scattering by anisotropic molecules.

Extensions of the Rayleigh formula.—The same method leads to two new generalizations. The first theoretically applies to *resonance scattering*, and, in a special case, is equivalent to a formula derived by Lamb. The second applies to scattering by a gas which contains active *molecules of more than one type.*

The relation of scattering to opacity is briefly discussed. A *partial bibliography* is included, of Rayleigh scattering and of opacity in general. The standpoint throughout is that of classical theory; the quantum theory of scattering is not dealt with in this report.

1. *Molecular Scattering of Light.*—When light passes over a particle, such as a molecule in a gas, the particle becomes the source of secondary radiation, and is said to "scatter" the light. Since the energy of the scattered radiation is derived from the primary beam, the intensity of the latter is reduced by the process; thus each particle in an otherwise homogeneous, transparent medium contributes to the opacity. Since, furthermore, the phase of the resultant in the direction of propagation of the scattered and the original radiation usually is somewhat altered, each scattering particle influences the refractive index of the medium. The opacity coefficient, K, and the refractive index, μ, are quantities experimentally measurable; the theoretical problem is to describe the relation between them.

This problem was first outlined by Lord Rayleigh, in connection with the explanation of the blue color of the sky; and the classical theory of the molecular scattering of electromagnetic radiation centers about his notable formula,

$$K = \frac{32\pi^3(\mu-1)^2}{3N\lambda^4}, \qquad (1)$$

where λ is the wave length in vacuum of the radiation, and N is the number of molecules per unit volume. The opacity coefficient, K, due

to scattering, is such that, if I_0 is the incident intensity of monochromatic radiation, the intensity I in the direct beam after thickness x of the gas has been traversed, is

$$I = I_0 \epsilon^{-Kx}, \tag{2}$$

where ϵ is the base of natural logarithms.

2. *The Color of the Sky.*—An account of the various hypotheses which have been advanced in explanation of the blue of the sky has been given by Nichols.[1] Brücke's hypothesis[2] (1853), tracing indeed to Leonardo da Vinci, that the color of the sky was that of a turbid medium found confirmation in his own experiments and particularly in the laboratory demonstrations of Tyndall,[3] who showed that the light scattered from sufficiently fine fogs was predominantly blue in color. In 1871, Rayleigh put the matter on a secure theoretical basis, and in a series of papers,[4] extending over many years, he developed the theory of the scattering of radiation by small particles. The first laboratory proof that the gas molecules themselves (which Tyndall had supposed inefficacious) gave rise to such scattering was carried through by Cabannes (1915),[5] who was followed by Smoluchowski, and by R. J. Strutt, the present Lord Rayleigh.[6]

3. *The Limitations of the Rayleigh Formula.*—In describing the interaction of molecules and radiation, Rayleigh's original quantitative derivation (1899) made use of the special postulates of the elastic-solid theory of light, although he was careful to explain that this particular method was employed merely as an illustration, and that the electromagnetic theory was equally serviceable. The description furnished by the electromagnetic theory[7] of the nature of the active molecules, as well as that given by electron theory,[8] leads to the same result. Schuster has shown, indeed, that definite assumptions of this sort are superfluous, that the Rayleigh formula can be derived by employing

[1] E. L. Nichols, Physical Review, *26*, p. 497; 1908.

[2] E. Brücke, Poggendorf's Annalen, *88*, p. 363; 1853.

[3] J. Tyndall, Proc. Roy. Soc., *17*, p. 223; 1868. Phil. Mag., *37*, (4), p. 384; 1869.

[4] Lord Rayleigh, Phil. Mag., *41*, (4), pp. 107; 274, and 447; 1871; *12*, (5), p. 81; 1881; *44*, (5), p. 28; 1897; *47*, (5), p. 375, 1899; *35*, (6), p. 373; 1918. Reprinted in *Scientific Papers*.

[5] J. Cabannes, Comptes Rendus, *160*, p. 62; 1915; *171*, p. 852; 1920. Annales de Physique, *15*, p. 5; 1921; (an inclusive treatise).

[6] R. J. Strutt, Roy. Soc. Proc., *94* A, p. 453; 1918; *95* A, pp. 155 and 476; 1919; *97* A, p. 435; 1920.

[7] J. Kunz, Phil. Mag., *39*, p. 416; 1920.

[8] L. Natanson, Phil. Mag., *38*, p. 269; 1919; A. Somerfeld, "Atomic Structure and Spectral Lines," p. 533, (note 2), London, 1923.

only the general terminology of wave-theory. This demonstration is reproduced in 4 below.

Any derivation of the Rayleigh formula, however, is subject to the following restrictions as to the nature of the scattering particles. Clear statement of these is highly advantageous.

(a) Their size is small compared with the wave length.

(b) The direction of response in each particle is in the direction of "vibration" of the primary wave, whatever the relative orientation of the particles, which thus are supposed isotropic in this respect.

(c) The secondary wave emitted by each particle is of the simple type described by equation (4) below, as regards variation with distance and angle.

(d) All of the active particles are alike.

(e) Their number per cubic wave length is not too great.

(f) They are arranged in highly irregular order, and possess large thermal movements.

(g) The impressed frequency (that is, of the initial beam), is not so near a "natural frequency" of a particle as to lead to a difference in phase at the particle appreciably departing from O or π between the scattered and the primary radiation.

Any or all of these restrictions may be removed by suitable mathematical refinement, and corresponding generalizations of the Rayleigh formula derived; the problems which thus arise are among the most interesting in theoretical physics. The present report brings together several such generalizations, two of which are believed to be new. This compilation is justified as a matter of convenience, and in addition the treatment clearly brings out the fact that specialized assumptions (of electron theory, etc.,) as to the nature of the interaction between molecules and radiation are superfluous, not only in the derivation of the limited formula, but also as regards the generalized formulas. Only the general terminology of wave theory is employed throughout.

Thus 5 presents from this view point the derivation of the well-known Einstein-Smoluchowski formula, which may be regarded as the generalization of the Rayleigh formula which results from the removal of restriction (e) above.

In 6, the case is treated which has been studied, among others, by Cabannes and by King, namely, scattering by non-isotropic molecules. This case leads to formulae free from restriction (b).

In 7, the result of the removal of restriction (g) is considered, and a new generalization of the Rayleigh formula is derived, which theoreti-

cally is valid for resonance-scattering. The resultant formula, in a special case, is shown to be equivalent to an equation worked out by Lamb.

In 8 the consequences of the removal of restriction (d) are studied. The limitation of the ordinary formula to scattering by identical molecules does not appear heretofore explicitly to have been stated.

The Rayleigh formula is susceptible of still other generalizations—in particular as regards restrictions (a) and (c).

In the present report the partially developed quantum theory of scattering is not touched upon. The classical theory of scattering is far from satisfactory in certain respects; and the application of the methods of quantum theory may be expected to lead to interesting developments; nevertheless, the success of the classical treatment is such that a too hasty abandonment of its view point would be highly inadvisable.

4. *Schuster's Derivation of the Rayleigh Formula.*—Let[9]

$$Z = Z_0 \cos \frac{2\pi}{\lambda}(ct - x)$$

represent the displacement (light vector) in the primary radiation, supposed monochromatic, plane-polarized, and travelling along the x axis in a plane-parallel beam; where c is the velocity of light, λ the wave length in vacuum, and t represents time. Then, supposing that restrictions (a), (b), and (c) above are satisfied, general wave theory shows that the scattered radiation, at (not too small) distance r from a single particle in the direction making the angle θ with the primary vibration, possesses the displacement,

$$z = \frac{Z_0}{r} \sin\theta \left[A \cos \frac{2\pi}{\lambda}(ct - x_1 - r) + B \sin \frac{2\pi}{\lambda}(ct - x_1 - r) \right] ; \qquad (4)$$

where x_1 is the coordinate of the particle; and A and B are quantities the values of which depend only upon the nature of the particle and the wave length of the light. The displacement z is directed perpendicularly to the line r, and lies in the plane determined by r and Z. This equation is equivalent to

$$z = \frac{Z_0}{r} \sin\theta \sqrt{(A^2 + B^2)} \cos \left[\frac{2\pi}{\lambda}(ct - x - r) + \phi - \frac{\pi}{2} \right] , \qquad (5)$$

where

$$\cot \phi = B/A \ .$$

[9] A. Schuster, "The Theory of Optics," 2nd edition, p. 325, 1909; 3rd edition, p. 320, 1924.

Since the intensity is proportional to the square of the amplitude, the intensity of radiation scattered from a single particle in the direction defined by θ is at the distance r,

$$S = I\frac{(A^2+B^2)\sin^2\theta}{r^2}, \tag{6}$$

where I is the intensity of the primary radiation (that is, the energy passing per unit time through unit area perpendicular to the primary beam). In consequence of restriction (g) above, B^2 is to be neglected in comparison with A^2.

The next step in the demonstration is devoted to the establishment of relations connecting, respectively, A with the refractive index, μ, of the gas, and B with the opacity-coefficient. Consider the effect, at some point O which is at the distance p, of the particles which occupy a thin stratum at right angles to the direction of propagation and of thickness dx. By the well-known method of Fresnel zones (and introducing a factor $2/\pi$ to allow for phase-variation) the total effect of this layer can be shown to be equal in magnitude to that which would be produced by a plane element of area $p\lambda$ lying at right angles to a line running to O and at a distance $p+\lambda/4$. Since such an element contains $Np\lambda dx$ particles, (where N is the number per unit volume), (4) indicates that the resultant at O of all the secondary vibrations which issue from the stratum dx is

$$z = Z_0\left[A\sin\frac{2\pi}{\lambda}(ct-p) - B\cos\frac{2\pi}{\lambda}(ct-p)\right]\lambda N dx .$$

To this must be added the expression for the primary wave itself, supposed to advance undisturbed, viz.,

$$Z = Z_0\cos\frac{2\pi}{\lambda}(ct-p) ;$$

and the resultant represents the displacement at O as modified by the particles in the stratum dx. The term in B indicates a diminution in amplitude, while the term in A indicates a change in phase. This resultant may be represented by

$$(1-k)Z_0\cos\frac{2\pi}{\lambda}(ct-p-\delta) .$$

Here δ is the retardation due to the particles, or

$$\delta = (\mu-1)dx ;$$

and k is the proportional diminution in amplitude caused by the scattering, or $Kdx/2$. Consequently, since dx is small,

$$k = NB\lambda dx$$

$$K = 2NB\lambda\ ; \tag{7}$$

$$\delta = NA\lambda^2 dx/2\pi\ ,$$

$$A = 2\pi(\mu-1)/N\lambda^2\ . \tag{8}$$

(In the equation for K an obvious misprint in Schuster's book has been corrected.) It is evident from (7) that the inclusion in (4) of the term in B is required if the condition of conservation of energy is maintained.

It is only in the direction of the primary beam that the scattered rays can combine together in so regular a manner as to justify the addition of displacements implied in (7) and (8); for only in this direction is the constantly shifting position of the particles due to the assumed thermal agitation without effect on the ultimate phase of the disturbance at a given point. The phase relations among the rays scattered in other directions are random; thus, returning to (6), the intensity of the scattered radiation due to all the particles in unit volume is got by adding the intensities due to each particle separately provided restriction (e) is satisfied. Consequently, with the aid of (8), the intensity of the radiation scattered at angle θ with the direction of the primary vibration, from all the particles in unit volume, is

$$S = \frac{4\pi^2(\mu-1)^2}{N\lambda^4}\,\frac{\sin^2\theta}{r^2}\,I\ . \tag{9}$$

Thus, as implied by (4), there is no scattered ray in the direction of the primary vibration.

Integrating over the surrounding spherical surface; with area-element $2\pi r^2 \sin\theta\ \mathrm{d}\,\theta$, gives for the total energy scattered per second per unit volume of the gas

$$S = \frac{32\pi^3(\mu-1)^2}{3N\lambda^4}\,I\ . \tag{10}$$

Since by (2) KI is the energy scattered per unit time per unit volume, (1) follows immediately from (10). Since $\mu-1$ is small, $4(\mu-1)^2$ is in the formulas occasionally written as (μ^2-1).[2]

In employing (9) it is to be remembered that the direction of vibration is perpendicular to the plane of polarization, and, of course, to the direction of propagation. If the primary radiation is unpolarized, the intensity of the scattered radiation in the direction making the

angle Φ with the primary beam is got by substituting $(1+\cos^2\Phi)/2$ for $\sin^2\theta$ in (9); and (10) remains unaltered. Thus (9) becomes

$$S' = \frac{4\pi^2(\mu-1)^2}{N\lambda^4}\,\frac{(1+\cos^2\Phi)}{2r^2}\,I\,. \tag{11}$$

Furthermore, (9) requires that the radiation scattered at right angles to the primary unpolarized beam be completely polarized in the plane determined by the two beams.

It is a consequence of these equations that if a fluid of refractive index μ, contains in suspension n small particles per unit volume; each of refractive index $\mu(1+\gamma)$, the opacity coefficient due to the scattering by the particles is

$$K = \frac{32\pi^3}{3}\,\frac{nv^2\gamma^2}{\lambda^4/\mu^4}\,, \tag{12}$$

where v is the volume of each particle. This is an obvious corollary of (1), in view of the fact that the resultant refractive index, relative to that of the homogeneous fluid, is $1+\eta v\gamma$, while the wave length is reduced in the fluid to λ/μ.

5. *The Einstein-Smoluchowski Formula.*—In a vapor near its critical temperature, the amount of scattering is far greater than the Rayleigh formula indicates. It was pointed out by Smoluchowski[10] that, in consequence of the thermal molecular agitation, accidental deviations of density arise in a vapor which may greatly increase its scattering power. For the calculation of this effect Einstein[11] employed Boltzmann's entropy probability principle and Maxwell's equations; the following less rigorous argument leads nevertheless to Einstein's final result.

Consider the fluctuations in density, about the mean demanded by the conditions of statistical equilibrium, of a tiny volume element, v, of a gas; this volume element is supposed small compared with λ^3, but yet large enough to contain many thousand molecules. Representing the gas pressure by p, the mechanical work required to compress these molecules into a slightly smaller volume, $v-\delta v$, obviously is, to the second order of small quantities,

$$\delta A = p\delta v + \tfrac{1}{2}\frac{dp}{dv}(\delta v)^2\,.$$

[10] M. v. Smoluchowski, Annalen der Physik, *25*, p. 205; 1908.
[11] A. Einstein, Annalen der Physik, *33*, p. 1275; 1910.

Of this by far the larger amount, $p\delta v$, is supplied by the expansion of the surrounding gas; the remaining (second order) quantity of energy is supplied as a result of the random departure from the condition of exact equilibrium. As a consequence of Boltzmann's theorem, representing by $\overline{(\delta v)^2}$ the mean value of $(\delta v)^2$, it can be shown that

$$\tfrac{1}{2}\frac{dp}{dv}\overline{(\delta v)^2}=\tfrac{1}{2}RT\,, \tag{13}$$

where T is the absolute temperature of thermal equilibrium and R is the gas constant per molecule.

As a result of the compression corresponding to δv, the index of refraction of the volume element v of gas is increased in the ratio $1+\gamma$; and in consequence of the well known general (Mosetti-Lorentz) relation of the refractive index to density, namely,

$$\frac{\mu^2-1}{\mu^2+2}=b/V \tag{14}$$

where V is the specific volume, or the volume per unit mass, and b is constant—the value of γ readily may be shown to be given by

$$\gamma=\frac{(\mu^2-1)\,(\mu^2+2)}{6\mu^2}\,\frac{\delta v}{v}\,. \tag{15}$$

(The Mosetti-Lorentz relation doubtless could be derived from general postulates of wave theory.) There are per unit volume $n=1/v$ such volume elements, v; consequently (12) gives for the opacity coefficient due to scattering as the result of these density variations,

$$K=\frac{32\pi^3}{3}\,\frac{v\mu^4\overline{\gamma^2}}{\lambda^4}\,, \tag{16}$$

where $\overline{\gamma^2}$ is the mean value of γ^2. Eliminating δv through (13) and (15), and combining the resultant equation for γ^2 with (16) leads to

$$K=\frac{8\pi^3}{27}\,\frac{\beta RT(\mu^2-1)^2(\mu^2+2)^2}{\lambda^4}\,, \tag{17}$$

where β is the compressibility of the substance, or $-(dv/dp)/v$.

This is the Einstein-Smoluchowski formula for opacity due to scattering. It is more general than the Rayleigh formula, and reduces to the latter for a gas obeying Boyle's law; since in that case $\beta=1/p=1/NRT$, where N, as in (1), is the number of molecules per unit volume; and $\mu^2+2=3$, very nearly. For a substance having a pressure, volume

relation such that the pressure increases less rapidly than Boyle's law demands, the value of β is greater, and thus the scattering more intense. As Smoluchowski has stated, the effective index of refraction of a substance is not increased to the same extent by the random variations in density; for it is given by $1+\Sigma\gamma v$, and the algebraic sign of γ is positive for some volume elements and negative for others.

There is nothing in the derivation of (17) which confines its application to gases and vapors; it is indeed known to apply to liquids.

Einstein's rigorous derivation involves, at an intermediate stage, the yet more general equation

$$K=\frac{RT}{6\pi}\left(\frac{2\pi}{\lambda}\right)^4\frac{V\left(\frac{\partial\mu^2}{\partial V}\right)^2}{\frac{\partial^2\psi}{\partial V^2}}. \qquad (18)$$

Here V is the specific volume; and the function $\psi(V)$ represents the mechanical work involved in bringing the system from the condition of strict thermodynamic equilibrium to the condition indicated by V. For a homogeneous substance, $\psi=-\int pdV$, and, in consequence, also, of (14), (18) reduces to (17).

6. *Modification of the Rayleigh Formula for Anisotropic Molecules.*— The derivation in 4 of the Rayleigh formula is subject, as stated, to the restriction that each particle be isotropic as regards the setting up of the internal "vibrations." Rayleigh himself (1918)[4] indicated the first step toward the removal of this restriction; and the theory of scattering by anisotropic molecules has been developed by Cabannes[5] (1921), and by King.[12] Their demonstrations are slightly generalized here.

For an anisotropic molecule, the direction of response (or, in the more specialized terminology of the electron theory, the direction of the forced vibration of a dispersion electron) is not necessarily that of the displacement, Z, in the primary light wave; nor is the amount of response independent of the orientation of the molecule with respect to the "light vector." Accordingly, (4), neglecting the small term in B, may be generalized as

$$z=\frac{Z_0 a}{r}\sin\chi\cos\frac{2\pi}{\lambda}(ct-r)\ ; \qquad (19)$$

[12] L. V. King, Proc. Roy. Soc., *104* A, p. 333; 1923. Phil. Trans., *212* A, p. 375; 1922.

where a is the magnitude of a vector-quantity which characterizes the total response of the molecule to the vector Z of the polarized primary beam; and z represents the displacement, at the distance r from the particle, of the radiation scattered in the direction making the angle χ with the vector a. For a given molecule, having a given orientation with regard to Z, a may represent the resultant of a number of vectors a_n, each of which characterizes a particular response for the given orientation. The molecule is assumed small compared with the wave length, and the further assumption is made that there is no initial phase-difference requiring attention between primary and scattered radiation. In view, further, of the geometrical considerations involved, it is legitimate to employ in (19) only the resultant magnitude a.

Thus the total energy scattered per unit time from N similar particles in unit volume is

$$S=\frac{8\pi}{3}N\bar{a}^2I\,, \tag{20}$$

where I is the intensity of the primary beam, and $\bar{a}^2$ represents the value of a^2 averaged for all orientations of a single particle.

Writing a_1, a_2, a_3 as the magnitudes of the components of a along the x, y and z axes, respectively, and supposing as above that the vibration of the primary beam takes place along the z axis and is propagated along the x axis,

$$\begin{aligned} a_1&=\sum R_i n_i l_i\,, \\ a_2&=\sum R_i n_i m_i\,, \\ a_3&=\sum R_i n_i^2\,, \end{aligned} \tag{21}$$

where l_i, m_i, n_i are the direction cosines characterizing the *ith* response for a given orientation of a given molecule; and R_i is a quantity which depends upon the wave length of the light, but is independent of molecular orientation. The following relations can be shown to hold when averages are taken for all molecular orientations, regarded as equally probable. In the establishment of these relations only statistical considerations enter.

$$\overline{a_1}=\overline{a_2}=0\,, \tag{22}$$

$$\overline{a^2}=\overline{a_1^2}+\overline{a_2^2}+\overline{a_3^2}\,, \tag{23}$$

$$\overline{a_1^2}=\overline{a_2^2}\,, \tag{24}$$

$$3(\overline{a_3})^2=\overline{3a_3^2}-4\overline{a_1^2}\,. \tag{25}$$

In consequence of (22), it is readily seen that (8) may be rewritten as

$$\overline{a_3} = 2\pi(\mu-1)/N\lambda^2 . \tag{26}$$

When the primary beam is unpolarized, the expression for the "depolarization" of the beam scattered at right angles to the direction of propagation of the primary radiation is, in view of (24),

$$\rho(\pi/2) = \rho = 2\overline{a_1^2}\,/(\overline{a_1^2}+\overline{a_3^2}) . \tag{27}$$

By the "depolarization," $\rho(\Phi)$, is meant, in general, the ratio of the intensity of the weaker to the intensity of the stronger component (as regards polarization) of the radiation scattered in the direction making the angle Φ with that of the primary beam. The stronger component is polarized in the plane determined by the directions of the primary and scattered beams; the weaker is polarized in the plane perpendicular to this one. For isotropic molecules, in the notation of 4, $a_3 = \bar{a}_3 = A$; $\overline{a_3^2} = (\bar{a}_3)^2 = A^2$; $a_1 = a_2 = \overline{a_1^2} = \overline{a_2^2} = 0$; and thus $\rho = 0$.

When $\overline{a^2}$ is eliminated from (20) through (24), (25), (26), and (27), the resultant expression for $K = S/I$ is,

$$K = \frac{32\pi^3}{3}\,\frac{(\mu-1)^2}{N\lambda^4}\,\frac{6+3\rho}{6-7\rho} ; \tag{28}$$

and this is the Rayleigh formula generalized for the case of anisotropic particles. King has given other formulas of interest in this case. In particular, when the primary beam is unpolarized,

$$\rho(\Phi) = \rho + (1-\rho)\cos^2\Phi . \tag{29}$$

As Cabannes has pointed out, and as the demonstrations given here clearly indicate, the accuracy of all of these formulas for scattering depends only upon geometrical considerations and upon the validity of postulates of general wave theory concerning the nature of light and the nature of the molecular response to light. From this standpoint the additional special postulates of the elastic-solid theory, the electromagnetic theory, and the electron theory, are superfluous, and their introduction into the demonstration of the above formulae leads to unnecessary complication. (Quantum considerations may be another matter.)

7. *Extension of the Rayleigh Formula to the Case of Resonance-Scattering.*—The restriction (g) of 3 may readily be removed, by the following obvious extension of Schuster's treatment. For this case of

resonance scattering, Lamb[13] has developed, by complicated analysis, a formula for the opacity; he adopted the special terminology of electromagnetic theory, but stated that the result was a general one. Lorentz[14] and others have worked out similar equations from the standpoint of electron theory.

Returning to (6) in 3, E^2 was neglected in comparison with A^2, in conformity with restriction (g). When E^2 is not thus neglected, the opacity coefficient due to scattering—gotten by integrating (6) through the total solid angle and comparing the result with (2)—comes out, in the notation of 3,

$$K=\frac{8\pi}{3}N(A^2+B^2)\,. \tag{30}$$

The three independent equations, (7), (8), (30), permit the elimination of any two of the four quantities, A, B, K, μ. An additional equation easily is obtainable which involves the ϕ of (5); namely,

$$B/A=\cot\phi=K\lambda/4\pi(\mu-1)\,. \tag{31}$$

Here $\pi/2-\phi$ is the phase-retardation of the scattered light.

Substituting in (30) the value for A of (8),

$$K=\frac{32\pi^3}{3}\,\frac{(\mu-1)^2}{N\lambda^4}\csc^2\phi\,; \tag{32}$$

and this reduces to the ordinary Rayleigh form when ϕ is near O or π.

Equations (31) and (32) lead to the following relation, more general than that of Rayleigh, between the opacity coefficient due to scattering and the corresponding index of refraction.

$$K\lambda/4\pi=\alpha\pm\{\alpha^2-(\mu-1)^2\}^{\frac{1}{2}}\,, \tag{33}$$

where

$$\alpha=\frac{3}{16\pi^2}N\lambda^3\,.$$

When $(\mu-1)/\alpha$ is small, (33) becomes the ordinary Rayleigh formula if the minus sign is employed. If the plus sign is employed (33) gives

$$K_m=\frac{3}{2\pi}N\lambda^2\,, \tag{34}$$

which is Lamb's value for the simplest case, when the impressed frequency is practically coincident with a natural frequency.

[13] H. Lamb, Cambridge Phil. Soc. Trans., *18*, p. 348; 1899. (Stokes Commemoration.)

[14] H. A. Lorentz, Proc. Amsterdam Academy, *8*, p. 591, 1905; *18*, p. 34; 1914. L. Page, Astrophysical Journal, *52*, p. 65; 1920. J. Q. Stewart, Astrophysical Journal, *59*, p. 30, 1924.

From (7), (31), and (32),

$$K = \frac{3}{2\pi} N\lambda^3 \cos^2\phi \ ; \tag{35}$$

$$\mu - 1 = \frac{3}{8\pi^2} N\lambda^3 \sin\phi \cos\phi \ . \tag{36}$$

The above treatment, beginning with equation (4), is invalid if the number of active particles per cubic wave length is so great that the effect of these secondary sources is comparable in magnitude with that of the primary radiation. In that case an additional term must be added to Z_0 in (4), just as, when this problem is treated from the standpoint of electron theory, a term dependent on the "polarization" of the medium is added to the electric field of the primary radiation.*

The relation of ϕ to the frequency of the incident radiation is not given by the preceding argument; but, for convenience, the relation given by classical methods is stated here in general terms. When the frequency of the incident radiation is low, compared with the "resonance frequency" of the molecules, ϕ is very slightly less than $\pi/2$; $csc\phi$ is near unity, and (32) reduces to the Rayleigh form; while $\mu - 1$ possess a small positive value. When the frequency of the incident radiation is high, ϕ is slightly greater than $-\pi/2$, $\mu - 1$ possesses a small negative value, and (32) again takes the Rayleigh form. When, on the other hand, the impressed frequency is very close to the resonance frequency, ϕ is near zero, as is $\mu - 1$; and K takes on approximately its maximum value, that of (34). The maximum departure of μ from unity occurs when ϕ is $\pm\pi/4$; then $\mu - 1$ is $\pm 3N\lambda^3/16\pi^2$, and K possesses half its maximum value.

These results are consequences of the assumption that each scattering particle acts as a simple linear oscillator; with this assumption, elementary electron theory leads to the relation,

$$\tan\phi = \frac{\lambda_0}{\pi a} e^{2\beta} \sinh\beta \ ; \tag{37}$$

where a is the "electromagnetic radius" of the electron (or $2e^2/3mc^2$, with the usual symbols), λ_0 is the wave length of resonance; and β is given by

$$\lambda = \lambda_0 e^{\beta} \ ,$$

where λ is the wave length of primary radiation. The vibrating electron is supposed subject only to the damping due to its own radiation,

* Doppler effect of heat-molecular agitation is also neglected.

calculated in the classical manner. Since the value of a is about 2×10^{-8} cm, the indicated "tuning" is very sharp.

8. *Modification for Particles of Several Types.*—This case, (which apparently has not heretofore explicitly been studied) results from the removal of restriction (d) in 3 above. When per unit volume there are $N\omega_1$ particles of type 1, $N\omega_2$ of type 2, etc. (where N is the number per unit volume of particles of all types), equations (7) and (8) are replaced respectively by

$$K=2N\lambda\sum\omega_iB_i\ ,$$
$$\sum\omega_iA_i=2\pi(\mu-1)/N\lambda^2\ ;$$

while the total energy scattered per second per unit volume of the medium is

$$KI=\frac{8\pi}{3}NI\sum\omega_i(A_i^2+B_i^2)\ .$$

Each summation is taken over all the particles, and

$$\sum\omega_i=1\ .$$

In these equations, K and μ refer to the resultant values for the composite medium. Accordingly, writing K_i and μ_i for the opacity coefficient and refractive index, respectively, which would be due to the $N\omega_i$ particles of type i, acting alone,

$$K=\sum K_i\ ;\quad \mu=\sum\mu_i\ . \tag{38}$$

That is to say, the effect of each group of particles is independent of the others. This conclusion is indeed a consequence of the assumption, implied in restriction (e), 3, that each scattering particle functions independently of the others.

Write

$$\cot\phi_i=B_i/A_i;$$
$$\zeta=\sum\omega_i\cos^2\phi_i=\omega\cos^2\phi\ ; \tag{39}$$
$$\eta=\sum\omega_i\sin\phi_i\cos\phi_i=\omega\sin\phi\cos\phi\ ;$$

defining δ, η, ω, and ϕ. Thus

$$\cot\phi=\zeta/\eta\ ; \tag{40}$$
$$\omega=(\eta^2+\zeta^2)/\zeta\ . \tag{41}$$

Then, in view of (38), (35), and (36), the appropriate generalization of the Rayleigh formula is readily shown to be

$$K=\frac{32\pi^3}{3}\ \frac{(\mu-1)^2}{N\omega\lambda^4}\cos^2\phi\ . \tag{42}$$

In terms of K and μ, cot ϕ is given, as before, by (31). Equation (42) thus differs from the previous formula, (32), only in the presence of $N\omega$ in place of N. When all the active particles are of one type, (41) and (39) show that ω is unity, and (42) reduces to (32).

If scattering is due to resonance at wave lengths λ_i which are short compared with λ, (37) gives

$$\cos\phi_i = 2\pi a\lambda_i^2/\lambda^3 ;$$

and cos ϕ_i is small. Substitution in (41) gives, approximately,

$$\omega = \frac{[\sum\omega_i\lambda_i^2]^2}{\sum\omega_i\lambda_i^4} , \tag{43}$$

nearly. In this case, ω is independent of ϕ; furthermore, if the various values, λ_i, are of the same order of magnitude, ω is near unity.

The observational fact, that the ordinary Rayleigh formula quantitatively describes, to a first approximation, scattering by atmospheric air (which is of course a mixture of gases) indicates that these conditions hold for air.

9. *Experimental Verification of Above Formulas.*—This report is not concerned with the large amount of experimental work which has been done in connection with the verification of these various classically derived formulas for scattering. It may be said, however, that those of 4, 5, 6 have found observational confirmation. The observations of Strutt and of Cabannes have been referred to above. The Rayleigh formula has received additional observational verification in connection with study of the transmission of solar radiation through the earth's atmosphere.[15] The Einstein-Smoluchowski formula has been tested by Raman, Ramanathan, and others.[16]

The validity of the formulas of 7 is more doubtful; quantitative data bearing on resonance scattering are difficult to obtain in the laboratory, and, on the theoretical side, quantum considerations require especial attention.[17] However, these formulas appear to be valid as regards the scattering of Hertzian waves by radio oscillators; and, even when specialized by the introduction of additional postulates of electron theory, they are in general accord with what optical data are

[15] F. E. Fowle, Astroph. Journ., *38*, p. 392; 1913; *40*, p. 435; 1914. H. Dember, Ann. der Physik, *49*, p. 549; 1916.

[16] C. V. Raman and K. R. Ramanathan, Phil. Mag., *45*, pp. 113, and 213; 1923. K. R. Ramanathan, Proc. Roy. Soc., London, *102* A, p. 151; 1922.

[17] E. A. Milne, Monthly Notices of R. A. S., *85*, p. 111; 1924. J. C. Slater, Amer. Phys. Soc., Abstracts of 130th meeting, no. 55, 1924; Physical Review; 1925.

available.[18] Resonance scattering was first observed by R. W. Wood.[19] Quantitative observations have been made by Füchtbauer and his collaborators.[20]

10. *General Considerations Relating to Opacity.*—It is necessary to make a distinction between opacity as regards the direct beam and opacity as regards total transmitted radiation. Equation (2), above, applies to the direct beam. When scattering is an important factor, the transmitted beam, after a small thickness has been traversed, may consist almost entirely of scattered radiation, and thus be much more intense than (2) would indicate.

The formula for the total emergent intensity then depends upon the geometrical arrangements, inasmuch as these affect the net "leakage" of radiation sidewise from the transmitted beam. In the simplest case—that of transmission by a plane parallel block of the medium, of finite thickness and infinite area—the emergent intensity I_2 is related to the initial intensity τ_1 by the following formula, due to Schuster,[21]

$$I_2 = \frac{I_1}{1+Kx} \tag{44}$$

where K is the opacity coefficient due to scattering, as defined by (2), and x is the thickness traversed.

Still another complication results when it is necessary to take into account the emissivity of the transmitting medium due to temperature radiation. The general equation for the transmission of radiation is

$$\frac{dI}{ds} = -KI + E\,, \tag{45}$$

where I is the incident intensity along ds, K is the total opacity coefficient due to all the processes involved in the given case, and E is the intensity along ds emitted per unit volume of the medium; E includes radiation scattered as well as radiation emitted due to temperature.[22]

Another aspect of the general problem of opacity relates to the various processes effective in producing opacity. Very often, and

[18] R. C. Tolman, Phys. Rev., *23*, p. 693; 1924.

[19] R. W. Wood, Phil Mag., *23*, p. 689; 1912; etc.

[20] C. Füchtbauer, P. Z., *12*, p. 722; 1911; P. Z., *21*, pp. 322 and 635, 1920; Füchtbauer and Hofmann, P. Z., *14*, p. 1169; 1913; Ann. der Physik, *43*, p. 96; 1924; Füchtbauer and Schell, P. Z., *14*, p. 1164; 1913; H. Bartels, Ann. der Physik, *65*, p. 143; 1921; Füchtbauer, Joos, and Dinkelacker, Ann. der Physik, *71*, p. 204; 1913.

[21] A. Schuster, Astrophysical Journal, *21*, p. 1; 1905.

[22] M. Planck, "The Theory of Heat Radiation."

especially in the case of gases, scattering—near or far from resonance—is the chief factor; thus, there is good reason to believe that stellar Fraunhofer lines[23] are the result of the highly selective or "resonance" scattering described in 7. In an ionized gas, however, the free electrons may be particularly efficacious in producing opacity, through the transformation of radiant energy to thermal energy, a process of true "absorption." This process has been treated by Stewart[24] from the standpoint of classical theory, and by Eddington from that of quantum theory.[25]

Finally, no theory of scattering is complete which fails to take into account the negative decrement in frequency between primary and scattered radiation known as the "Compton effect."[26] Classical theory has as yet failed to suggest a satisfactory explanation of such degradation in frequency, although there is strong experimental evidence for its existence.

PRINCETON UNIVERSITY OBSERVATORY,
PRINCETON, N. J.

[23] J. Q. Stewart, Monthly Notices of R.A.S., June, 1925.
[24] J. Q. Stewart, Phys. Rev., *22*, p. 324; 1923.
[25] A. S. Eddington, Monthly Notices of R.A.S., *83*, pp. 32 and 98, 1922; *83*, p. 431, 1923.
[26] A. H. Compton, Phil. Mag., *46*, p. 807; 1923, etc.

Facts about electrical Conduction produced in Crystals by Cathode Rays and Light.—Scattered observations, some of which are as follows: (a) A crystal of ZnS, exposed simultaneously to a P.D. of some 1000 volts between its sides and to a bombardment of 10 000-volt electrons upon one side conducts a current during the bombardment; this current is of about the same order of magnitude as that produced by illuminating the crystal instead of bombarding it. Quartz is not thus affected either by bombardment or by illumination. In these experiments the crystal must be plated with a very thin (transparent) but conductive layer of metal, to carry off the excess electrons (?) (b) The conduction produced by illuminating ZnS sinks very rapidly when the temperature is lowered and becomes quite imperceptible at about 135° K, remaining so down to the limit of observation at 82° K; the conduction so produced in diamond sinks to a value independent of temperature from 135° to 82° K.—[H. Lenz; Phys. ZS., *26*, pp. 365-368; 1925.]

KARL K. DARROW

Absorption Bands of Oxygen in the Ultraviolet.—This paper contains a tabulation of bands observed in the absorption-spectrum of oxygen between 1800 and 2200A. One set of bands appears when the oxygen is at room-temperature, and therefore is supposed to correspond to transitions from a normal state of the molecule, in which the atoms are not oscillating within the molecule; others appear consecutively as the temperature is raised, and correspond to initial states of consecutively greater amplitudes of oscillation. These experiments, therefore, indicate the same thing as the experiments on line absorption spectra which show that a given line is not absorbed until the atoms are put into the necessary initial state. An analysis of this band spectrum, not given in detail, indicates that the oscillation frequency of the atoms is 3 times as great before the absorption process as after it—an unprecedently large ratio, suggesting that the absorption of light effects what the authors call a pronounced "loosening" of the forces holding the atoms together in the molecule. The authors also detect some lines in the ultraviolet absorption spectrum of iodine near 2000A, with indications of a series.—[C. Fuchtbauer and E. Holm, Rostock; Phys. ZS., *26*, pp. 345-349; 1925.]

KARL K. DARROW

STUDIES IN LUMINESCENCE*

By Dorothy G. Engle and B. S. Hopkins

I. OBJECT AND METHOD OF WORK

The purpose of this investigation was to devise an apparatus to measure directly the intensity of luminescence, especially fluorescence; and to study luminescence and learn some of the properties and characteristics of this phenomenon. The first was done by an apparatus involving the use of a photoelectric cell. To study luminescence, a large number of series of samples were prepared and were measured by this method.

II. USE OF PHOTOELECTRIC CELL FOR MEASURING LUMINESCENCE

Most of the methods for measuring luminescence have been those of comparison. Optical pyrometers have been used, and other methods in which the luminescent light is compared with a standard light or with a standard sample of phosphorescent zinc sulphide[1,2]. The use of the photoelectric cell proved to be a very satisfactory method for measuring luminescence, and though the set-up is fairly complex after it is once arranged it remains constant for use.

Photoelectric Cell.—The photoelectric cell used in this work was of the type designed by Professor J. Kunz[3] and developed by him for stellar photometry. The cell made by him for this investigation was a caesium cell. This was chosen instead of any of the other alkali metals because it makes a cell which is more sensitive to that range of light which is visible to the human eye, and in this work it is the visible light that is of interest. The caesium cell is sensitive to light from wave length 409.5 mμ to 718 mμ.[4] Since the maximum visual intensity is about 535 mμ, the caesium cell furnishes a very convenient means for the accurate measurement of visible luminescence.

The Cell Box.—The container for the photoelectric cell was an especially prepared light-tight brass box with the proper fittings; as described in the literature.[4]

* Contribution from the Chemical Laboratory of the University of Illinois.

[1] Nichols, E. L., Sci., *55*, p. 157; 1922.

[2] Nichols, E. L., and Howes, H. L., J.O.S.A., *6*, No. 1, p. 42; 1922.

[3] Kunz, J., and Stebbins, J., Phys. Rev., *7*, (Ser. 2) p. 62; 1916.

[4] Seiler, E. F., Astrophys. J., *52*, No. 3, p. 129; 1920.

Cathode Ray Tube.—An apparatus for exciting samples quickly and easily by means of cathode rays was donated by Mr. W. S. Andrews. For operating this a good air pump,[5] which would give a vacuum of about 0.10 mm mercury. and an induction coil[6] were needed[7,8]. It required about 5 minutes to put a sample in and exhaust the tube.

Galvanometer.—The galvanometer used to measure the photoelectric current was a Leeds-Northrup high sensitivity type, having a figure of merit of 1.07×10^{-10}. A telescope fitted with a scale was used to read the deflections of the galvanometer.

Set-Up.—Through experimentation it was found that the best voltage for this particular cell and this work was between 130 and 140 volts. This was supplied by Radio B batteries. A resistance of 10,000 ohms was put in the circuit to safeguard against short-circuiting. It was found necessary to enclose all wires in heavy glass tubing which was well wound with tinfoil, to overcome the magnetic field set up when the induction coil was in operation.

Precautions.—The samples in each case were ground, not by any means powdered, so that the sample tray was entirely covered with uniform thickness; although it was found that the thickness of the layer had little effect on results, yet care must be taken that a uniform surface area is exposed.

Small differences in the cathode rays, depending on the degree of exhaustion of the tube and also on the induction coil spark, make very marked differences in both color and intensity of luminescence, so these conditions were kept uniform.

A galvanometer as sensitive as this work requires, must be kept carefully adjusted so the mirror will be absolutely free in swinging.

The pump, coil and cathode ray tube were on a separate table so their vibrations did not affect the galvanometer. This must, however, be very close to the cell box. Of course the distance between the cell and the sample must be kept constant, and also the angle between the sample and the opening of the cell box.

A drop in voltage in the main circuit produces a marked decrease in galvanometer deflections. So the voltage was adjusted as the batteries deteriorated.

[5] The pump used was a Cenco Hyvac, rpm 200-240, driven by a Cenco motor on a 110 volt current.

[6] The induction coil was a Thordarson Type 6, operated by a 6 volt current.

[7] Andrews, W. S., Gen. El. Rev., *28*, No. 2, p. 103; 1925.

[8] Andrews, W. S., Gen. El. Co. Private communication.

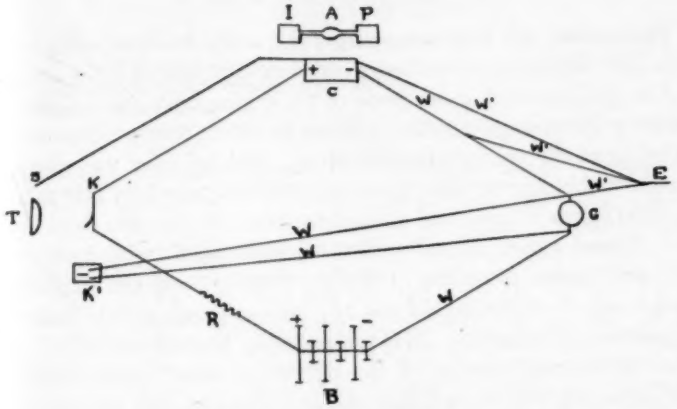

FIG. 1. *Set-up of apparatus*

FIG. 2. *Photograph of apparatus*

Key for diagram and photograph of set-up of apparatus.

A Cathode ray tube
B Batteries
C Cell box—cell inside
E Pipe to earth
G Galvanometer
I Induction coil
K Key for main circuit
K' Key to dampen galvanometer
P Air pump
R Resistance
S Cord on pulley to open and close shutter
T Telescope
W Wires in covered tubes
W' Wires for grounding

III. PREPARATION OF SAMPLES

Throughout this work the same general methods of preparing samples were used, different factors being varied as indicated in different series.[9]

Zinc Sulphide.—A good grade of phosphorescent zinc sulphide was made by dissolving 30 g zinc sulphate in 100 cc water. Ammonia was added until the precipitate redissolved. This solution was allowed to stand for about forty-eight hours to precipitate any iron that might be present; it was filtered, and allowed to stand another two days. It was then filtered again, diluted to 200 cc, made acidic with hydrochloric acid, and heated to boiling. Carefully purified hydrogen sulphide was passed into it to precipitate out any second group metals that might be present as impurities. This was carefully filtered and boiled. 10 cc of a .005 normal solution of the sensitizing agent[10] was added, and hydrogen sulphide passed into the hot solution, but not enough to precipitate all the zinc. This mixture was then poured into a solution of 200 cc cold water and 3 g sodium chloride. It was then filtered and dried without washing, and ground. This powder was heated at 800°C for about one hour.

The hydrogen sulphide was prepared from a Kipp generator, passing the gas through two wash bottles to purify it.

Calcium Metaphosphate.—Primary calcium phosphate was ignited with a trace of a rare element oxide, and fused to a clear bead of calcium metaphosphate.

$$Ca(H_2PO_4)_2 + \text{heat} \rightarrow Ca(PO_3)_2 + 2\ H_2O$$

Zinc Silicate.—These samples were prepared by dry fusions. 2 g zinc oxide, which had been freed from iron by ammonia, were mixed with 1.48 g silicon dioxide which had been prepared from sodium silicate and hydrochloric acid, boiling and washing the product with the acid till the solution no longer gave a test for iron. To this mixture was added a trace of rare element oxide as the sensitizer and all of it was mixed thoroughly. It was then heated at 1200°C for one-half hour.

$$ZnO + SiO_2 \rightarrow ZnSiO_3$$

Similar Compounds.—The compounds similar to zinc silicate were made in the same way, using correct proportions of the metallic oxide and the acidic oxide, and introducing a trace of a rare element oxide as the sensitizing agent. Extreme care was taken to purify all chemicals used and to keep them pure, especially free from iron.

[9] MacDougall, E., Stewart, A. W., and Wright, W., J.C.S. *111*, p. 663; 1917.
[10] Tanaka, T., J.O.S.A. *8*, No. 5, p. 659; 1924.

TABLE 1. *Effect of different sensitizers*

Voltage used in main circuit of caesium photoelectric cell.... .138
Galvanometer figure of merit.....1.075×10^{-10}
Distance from cell box opening to sample tray.....10 cm
Pressure in cathode ray tube.....0.13 mm

Sample	Sensitizing Agent	Fluorescence	Phosphorescence		Readings	
			Color	Duration sec.	Deflection[1] mm	Amperes ×10^{-10}
$ZnSiO_3$	No	white blue	dim	16	3	3.23
$ZnSiO_3$	MoO_2	bright green	very dim	6	16	17.20
$ZnSiO_3$	Mn	yellow green	dim	96	18	19.35
$ZnSiO_3$	Pr	bright blue	dim	16	26	27.95
$ZnSiO_3$	Tl	bright blue	dim	15	53	56.98
$ZnSiO_3$	Nd	bright blue	brighter	17	47	50.53
$ZnSiO_3$	Ce^{IV}	yellow green	brighter	78	42	45.15
$ZnSiO_3$	Yt^{I}	white	no	1	39	41.93
$ZnSiO_3$	YtII	bright green	dim	9	33	35.48
$ZnSiO_3$	YtIII	bright green	very dim	4	27	29.03
$ZnSiO_3$	MoO_3	blue	dim	33	33	35.48
Zn_2SiO_4	Cb	bright blue	blue	over 5min.	32	34.40
$ZnSiO_3$	Sa	bright blue	dim	11	16	17.20
$ZnSiO_3$	Sn	bright blue	dim	14	30	32.25
$Ca(PO_3)_2$	no	white	no	—	3	3.23
Ca $PO_3)_2$	MoO_3	green	no	—	25	26.88
$Ca(PO_3)_2$	Ce^{IV}	pale lavender	no	—	5	5.38
$Ca(PO_3)_2$	Er	pale pink	no	—	10	10.75
$Ca(PO_3)_2$	La	pale purple	no	—	7	7.53
$Ca(PO_3)_2$	Yt	pale pink	no	—	7	7.53
$Ca(PO_3)_2$	Nd	pale lavender	no	—	11	11.83
$Ca(PO_3)_2$	Sa	salmon pink	very slight	1	10	10.75
$Ca(PO_3)_2$	Cu	light blue	no	—	13	13.98
Calcite I[3]		yellow pink	yellow	over 5 min.	102	109.65
Calci e II		green and pink	salmon	78	22	23.65
Calcite III		yellow and green	yellow	6	41	44.08
CaS[4]		bright blue	purple	over 5 min.	43	46.23
ZnS	no	bright yellow	very dim	1	4	4.30
ZnS	Cu	yellow green	yellow	15	40	43.00
ZnS	Mg	blue green	white	34	43	46.23
ZnS	Mn	bright yellow	white	32	30	32.25
ZnS[4]	———	yellow green	yellow	over 5 min.	123	132.23
ZnS[4]	———	yellow white	yellow	ove 5 min.	63	67.73
Candle 9cm ×1cm — 65 cm away	———	———	———	———	3	3.23
Candle 9cm ×1cm — 45 cm away	———	———	———	———	15	16.13
Candle 9cm ×1cm — 20 cm away	———	———	———	———	23	24.73
Candle 9cm ×1cm — 18 cm away	———	———	———	———	27	29.03

NOTE: See footnote references to Table 1 at bottom of page 604.

IV. EFFECT OF SENSITIZING AGENTS

Qualitative.—Similar samples were made and tested, using traces of oxides of different metals as the sensitizing agent.

Quantitative.—The natural zinc silicates, such as willemite, have the composition $2ZnO \cdot SiO_2$. Experiments were made to see whether in the artificial compounds the orthosilicate, $2ZnO \cdot SiO_2$, or the metasilicate, $ZnO \cdot SiO_2$ show better luminescence. The following data were obtained, showing that the metasilicates are better, since in every experiment they give a higher deflection than the corresponding orthosilicates.

TABLE 2. *Comparison of ortho and meta silicates*

Sensitizing agent	Amount gram per 2 g ZnO	Deflection in mm Zn_2SiO_4	Deflection in mm $ZnSiO_3$
Nd_2O_3	.01	28	35
Nd_2O_3	.005	25	29
Nd_2O_3	.001	33	37
$Tl(NO_3)_3$	.01	46	52
$Tl(NO_3)_3$	.005	30	34
$Tl(NO_3)_3$	.001	40	44

A large number of experiments were made to determine the effect of different amounts of the same sensitizing agent in zinc silicates. It was found that the general curve is the same for different sensitizers. Figs. 3, 4, and 5 are the true curves for neodymium oxide, columbium oxide and ceric oxide, and thallium nitrate and molybdic oxide. The points on these curves are the results of several repetitions and checks, and those for neodymium and columbium oxides were entirely repeated on a new series of samples. The data obtained show that the intensity of luminescence, especially fluorescence, is periodic or rhythmic. This indicates that this phenomenon may be similar to straight periodic

[1] Deflection readings given here are the total deflections minus the deflections due to the cathode rays themselves and the small amount of light present in the room. They are the total deflections minus the "blank" deflections, so are the actual amounts produced by the light from the samples.

[2] Samples furnished by W. S. Andrews, General Electric Company.

[3] Samples of natural calcite from W. P. Headden, Fort Collins, Colorado.
I from Ingleside Quarry, Ingleside, Colorado.
II from Alford-Maxfield Quarry, near Fort Collins, Colorado.
III from Limestone Quar y, Murke, Wyoming.

[4] Samples of commercial products, from different companies.

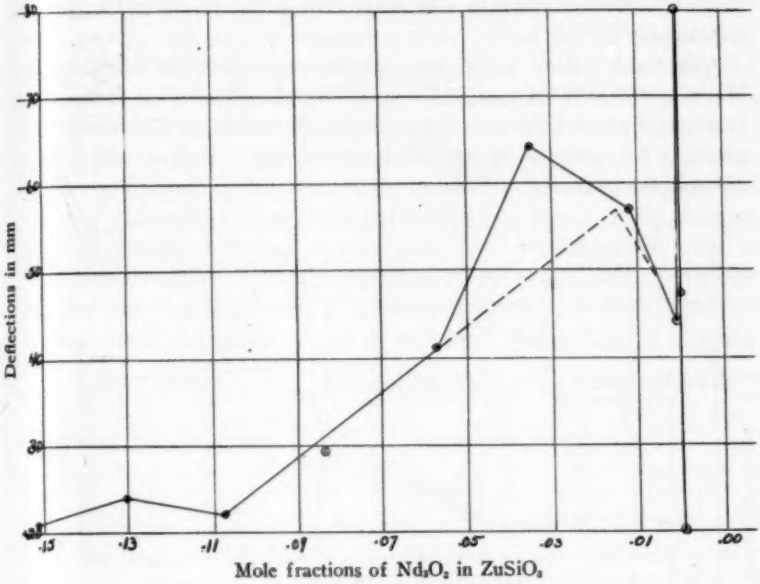

FIG. 3. *Amounts of Nd_2O_3*

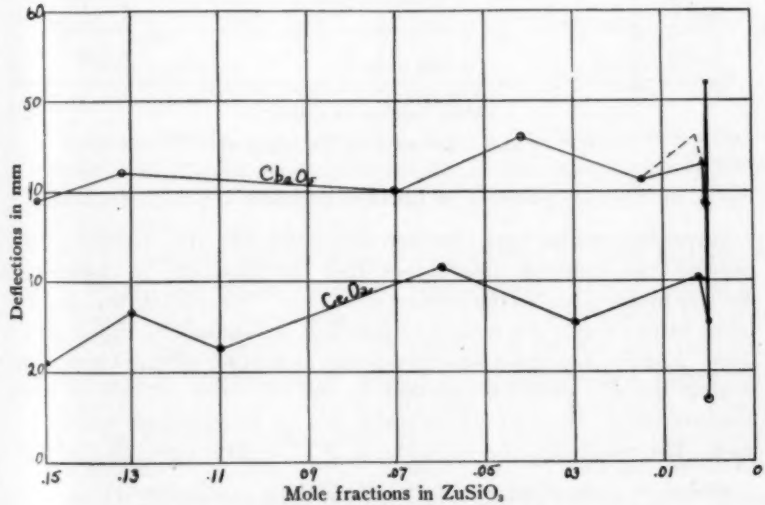

FIG. 4. *Amounts of Cb_2O_3 and CeO_2*

chemical reactions which are being found to be of quite general occurrence.[11,12,13]

Iron Oxide.—Iron has a very detrimental effect on luminescence. When a trace of ferrous or ferric oxide was added to a sample the luminescence was cut down to practically nothing. This shows the absolute necessity of having all chemicals free from iron and keeping all samples pure.

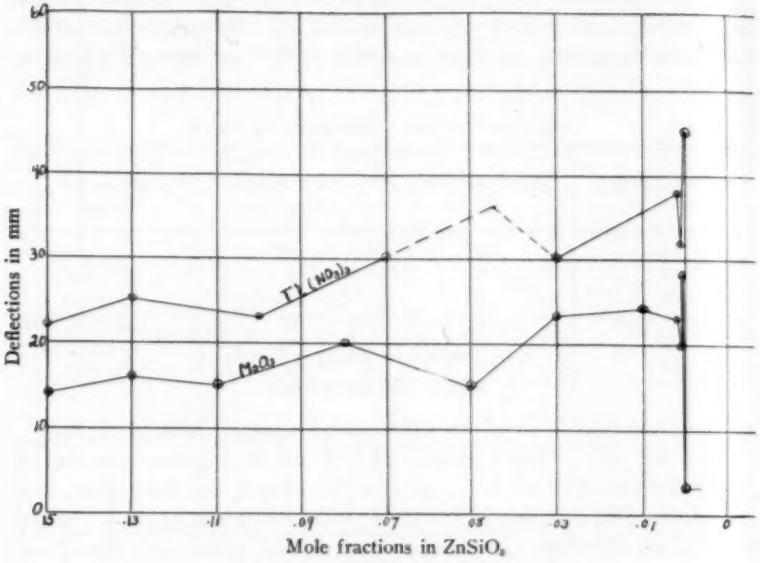

FIG. 5. *Amounts of $Tl(NO_3)$ and MoO_3*

V. EFFECT OF INTIMACY OF MIXTURE

Surprising results were obtained along this line also, partially disproving the common assumption that luminescence is somewhat directly proportional to the amount of mixing. This problem was undertaken in two ways, dry mixing or grinding, and liquid mixing or solutions. A series of samples was prepared by mixing for different intervals of time the zinc oxide, silicon dioxide and the small amount of neodymium oxide. These were then fused, and the luminescence was measured. The results are shown in Fig. 6, A. The next curve in Fig. 6 is

[11] Hedges, E. S., and Myers, J. E., J.C.S., *125*, p. 604, and p. 1282; 1924.
[12] Ostwald, W. Z. physikal. Chem., *35*, 33, p. 204, 1900.
[13] Bredig, G., and Weinmayr, I. Z. physikal. Chem., *42*, p. 601; 1903.

the curve for results obtained when the zinc oxide and silicon dioxide were fused and then the sensitizing agent added to the samples and mixed for increasing periods of time. Mixing was done by placing the material in tight bottles and rotating them on a wheel at 36 revolutions per minute for the different lengths of time. Similar experiments were made, grinding the samples instead of only mixing them. For this an improvised ball mill was used, made by placing iron-free marbles with the material in the bottles and rotating these. Curve C of Fig. 6 shows that the results of this set of experiments are practically the same as from mixing. Table 3, A shows the differences between mixing or grinding the samples before and after fusion. Table 3, B shows that the luminescence of a given sample is noticeably diminished by grinding.

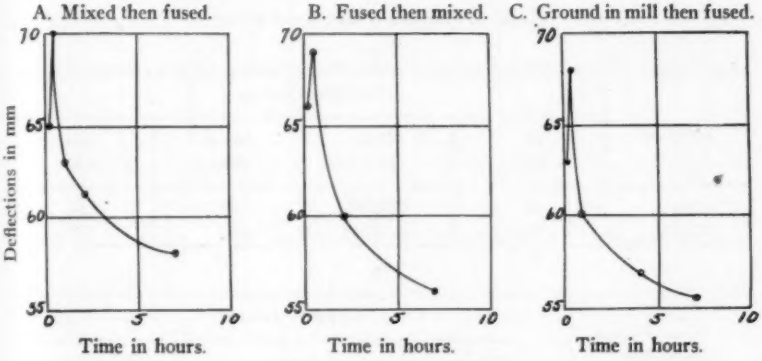

FIG. 6. *Effects of mixing*

If, after measuring, this is reheated, the original brightness is always restored and usually better than before. These experiments all show that continued dry grinding, mixing or crushing, is harmful after a relatively short length of time.

But intimacy of mixture when brought about by other methods is very effective in producing better luminescence. In the case of the sulphides, the best possible mixture was obtained by adding a soluble salt of the sensitizing agent to the solution of the zinc salt, then precipitating the sulphide in the usual way. Our experiments show that this method gives much better results than can be obtained by dry mixing of the sulphide and sensitizer. With the silicates better results were obtained when the nitrate of the sensitizing agent was used. When this is fused with the zinc oxide and the silicon dioxide it gives a liquid fusion and a much more intimate mixture. Samples prepared in this way

showed more luminescence then those prepared by mixing the three oxides and fusing them, since this fusion remains dry throughout.

VI. EFFECT OF TIME AND TEMPERATURE OF FUSION OF ZINC SILICATES

The intensity of the luminescence of zinc silicates is influenced both by the time of fusion and the temperature at which the heat treatment is carried out. A number of samples of zinc silicate were put in a furnace at 1150°C and were left in for different lengths of time. Similarly, a number of samples were heated for thirty minutes each, but at different temperatures. The results of these two sets of experiments are plotted (Figs. 7 and 8) showing the effect of time and temperature of fusion.

TABLE 3. *Relation of heating and mixing*

A

Sensitizer	Deflections in mm			
	Mix heat	Heat mix	Grind heat	Heat grind
CeO_2	68	53	45	34
Nd_2O_3	66	63	50	44

B

Sensitizer	Deflections in mm		
	Sample	Sample ground	Reheated
CeO_2	56	40	58
Nd_2O_3	53	36	54

VII. RATE OF DECAY OF LUMINESCENCE OF ZINC SILICATES

Data were obtained over a period of some time on the same samples to determine the change in luminescent properties due to age. The results of these experiments are plotted, Fig. 9 showing that the decay is fairly rapid for the first few days then gradually becomes almost zero.

A good sample of commercial luminescent zinc sulphide which was eleven years old was tested at various intervals during a year and showed no apparent change.

If we assume that luminescence is produced by a state of strain within the solid, these studies seem to indicate rather clearly that the state of strain is relieved by some sort of readjustment, the influence of

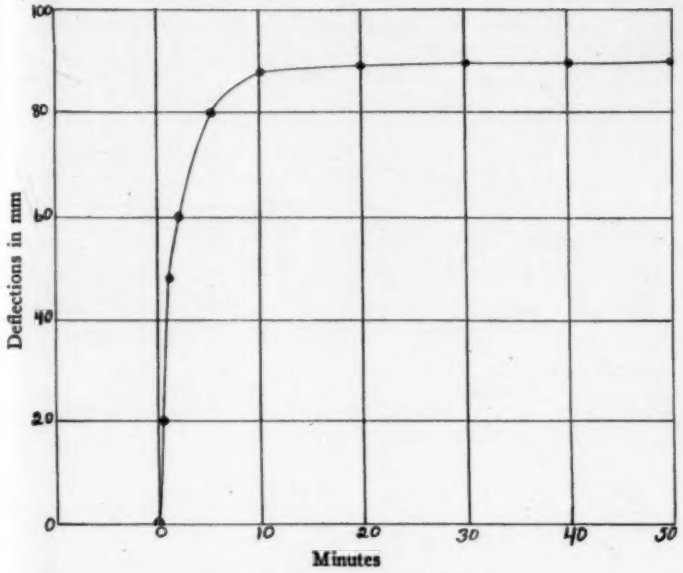

FIG. 7. *Time of fusion of zinc silicate*

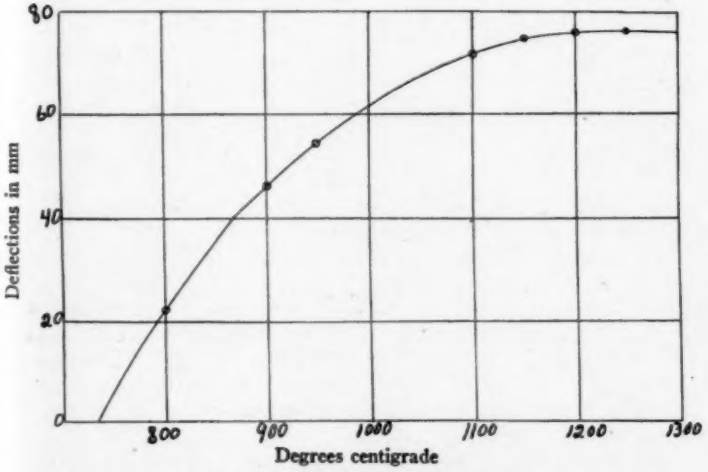

FIG. 8. *Temperature of fusion of zinc silicate*

which is marked at first but gradually decreases to a point at which an equilibrium is established. After this condition is reached, the age of the material seems to have little further effect on the luminescent properties of these compounds.

Comparison of a sample of zinc silicate which had been repeatedly excited with a parallel one of the same age which had been kept covered and protected from excitation showed that the first had a somewhat better luminescence. This would be expected since every time the sample is excited the physical state of strain is established which only slowly changes back to the more stable form.

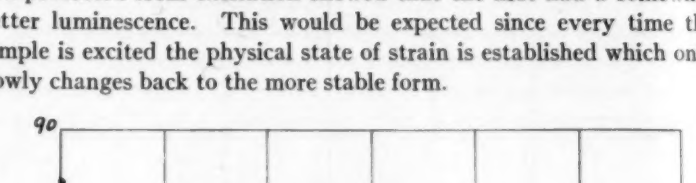

FIG. 9. *Rate of decay of luminescence of zinc silicate*

VIII. MICROSCOPIC STUDIES

Studying the samples under an average microscope indicated that the material, silicate or sulphide, is amorphous. At least no crystalline structure was detected with a telescope giving magnification of 150. But when studied with a much higher magnification, (970), using an oil immersion, a semi-crystalline structure was detected. This is in accordance with work previously reported on zinc sulphides.[14] Under the microscope our samples have shown three distinct states of aggregation. In some samples there was a preponderance of small amorphous particles, while in others these small particles had apparently coalesced into much larger amorphous masses. In addition there were certain particles which showed a definite tendency toward crystalline structure. Our experiments indicate that there is a definite relationship between the size of particles and luminescence. All of the most luminescent

[14] MacDougall, E., Stewart, A. W., and Wright, R., J.C.S., *111*, pp. 663-683; 1917.

Correction facing page 420, J. O. S. A. & R. S. I., October, 1925. Please paste this edge on page 421.

FIG. 1. *Type of galvanometer investigated. One instrument was constructed in the usual manner; in the other instrument the electrical circuit was entirely of copper.*

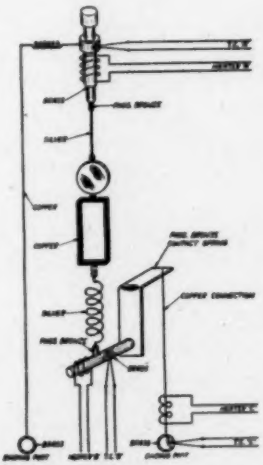

FIG. 2. *Diagrammatic sketch showing the various materials comprising the electrical circuit in the usual form of galvanometer. All these parts were made of copper in the all-copper circuit instrument.*

samples from various series showed particles of a fairly uniform size, while those samples in which the particles were either larger or smaller were not as luminescent. So far as we have been able to determine samples whose particles are small are lacking in crystalline structure while those composed of larger masses always show some tendency toward the formation of crystals. This observation offers an easy explanation to the fact that grinding decreases luminescence and that subsequent heating tends to restore it (Table 3).

IX. EFFECT OF LIGHTS OF DIFFERENT COLORS

For this group of experiments samples of commercial zinc sulphide and calcium sulphide were used, since these are easily excited by ordinary light. A set of ray filters was used[15] and the samples were exposed through these to lights from various sources. In this way the red, yellow, green, blue and violet light could be used separately from each of the sources. The results, shown in Table 4, were all practically the same irrespective of the source of light and show that the blue portion of the spectrum is best for exciting phosphorescence in these samples, with the green and yellow next in order.[16]

X. COLOR CHANGES IN FLUORESCENCE OF ZINC SILICATES

A wide range of colors and shades is possible in this field, by varying one of the several factors.

From Table 1 it will be seen that the nature of the sensitizer produces marked changes in the color of the luminescence, especially the fluorescence. The zinc silicates are all of a blue or green color, but the shades vary from yellow-green, bright green and bright blue to purple. With the calcium metaphosphates the colors may be green, lavender, pink, blue, purple, or white. The zinc sulphides are all varying shades of yellow and green. So in general the nature of the sensitizing agent changes the shade of the fluorescence.

The amount of the sensitizer also changes the shade of the fluorescent light very noticeably. The color increases from yellow to bright purple blue in the case of silicates and sulphides as the amount of the sensitizing agent decreases.[17,18,19] For the effect of the quantity of sensitizer and other conditions affecting color changes see Table 5.

[15] Regular glass filters—Wratten filters.
[16] Headden, W. P., A.J.Sci., *5*, p. 314; 1923.
[17] Headden, W. P., A. J. Sci., *6*, p. 247; 1923.
[18] Headden, W. P., Colo. Sci., Soc., *11*, p. 399; 1923.
[19] Tanaka, T., J.O.S.A., *8*, p. 287; 1924.

The temperature of fusion has its effect on color. The fluorescence of the silicates changes from yellow to bright blue with an increase in temperature. This is just opposite to the effect of temperature on zinc

TABLE 4. *Phosphorescence of CaS and ZnS when excited by lights of different colors*

Source	Red	Yellow	Green	Blue	Violet
Day Light					
CaS	none	none	none	fair	none
ZnS	none	none	poor	good	none
Sun Light					
CaS	none	none	none	good	none
ZnS	none	none	fair	good	none
Copper Arc[20]					
CaS	fair	poor	fair	good	poor
ZnS	poor	none	poor	very good	very poor
Iron Arc					
CaS	poor	poor	none	very good	very poor
ZnS	none	none	none	very good	none
Carbon Arc					
CaS	none	poor	very poor	very good	very poor
ZnS	none	poor	very poor	very good	none
Electric[21] Light					
CaS	none	none	none	poor	none
ZnS	none	none	none	fair	none
Mercury[22] Vapor					
CaS	very little	little	none	good	none
ZnS	none	very poor	fair	very good	none

[20] Arcs were all operated by 110 volts direct current.

[21] Electric light was a tungsten filament, nitrogen filled bulb, candle power 50 w and voltage 110.

[22] Mercury vapor lamp was in a quartz tube.

sulphides from work reported by MacDougall, Stewart and Wright,[14] who found that an increase of temperature caused the color of luminescence of zinc sulphides to shift toward the red end of the spectrum.

Our work indicates that in the case of zinc silicates the shift is toward the purple.

TABLE 5. *Color changes in fluorescence of zinc silicates*

Varying Factor	Yellow	Green	Blue	Purplish Blue	Bluish Purple	Purple
Time (Minutes)	5	10	15	20	25	30
Temperature (Degrees C)	800	950	1000	1100	1150	1200
Mole Fraction of Sensitizer (Nd_2O_3)	.1	.05	.01	.001	.0005	.0001

The time of fusion has the same effect, the color changing quickly from pale yellow to purple blue with increasing time of heating.

The source of the exciting light also has a marked effect upon the color of the fluorescence; this was discussed under the preceding topic under the experiment with ray filters.

TABLE 6. *Similar compounds*

Sensitizing agent.....Nd_2O_3
Amount of sensitizer.....01 g per 2 g base
Temperature of fusion.....1200°C
Time of fusion.....30 minutes

Compound	Fluorescence		Phosphorescence
	Color	Quality	
$BeSiO_3$	pale yellow	little	practically none
$MgSiO_3$	salmon	bright	fair
$CaSiO_3$	purple	very bright	very good
$ZnSiO_3$	purple	very bright	very good
$SrSiO_3$	blue	bright	very good
$CdSiO_3$	purple	good	excellent
$BaSiO_3$	blue	good	good
$HgSiO_3$	yellow green	bright	fair
$ZnTiO_3$	blue	very good	fair
$ZnZrO_3$	blue	very good	bright
$BeWO_4$	yellow	little	Practically none
$ZnWO_4$	yellow	little	very little

Lastly, according to previous work[23] the color of luminescence changes somewhat regularly with the atomic weights of the base used, the same sensitizer being used in all cases.

[23] Tanaka, T., J.O.S.A., *8*, No. 2, pp. 295-299; 1924.

XI. LUMINESCENCE OF SIMILAR COMPOUNDS

Since zinc silicates when properly prepared with sensitizing agents are very good in luminescence, the question naturally arises whether metals similar to zinc and elements similar to silicon will form luminescent compounds. Silicates were prepared of all the metals in Group II except radium; in addition certain titanates, zirconates and tungstates were made in the manner described for the silicates. The results are shown in Table 6.

XIII. SUMMARY

Experimental results show that:

1. A photoelectric cell is very satisfactory for measuring luminescence.

2. Zinc sulphides, calcium metaphosphates and zinc silicates are luminescent.

3. The best sensitizing agents for zinc sulphide are magnesium, copper and manganese. The best ones for calcium metaphosphate are molybdenum, neodymium and erbium; for zinc silicates the best are thallium, neodymium, ceric cerium, columbium, and molybdenum.

4. In general, luminescence increases with decreasing amounts of the sensitizing agent, although absolutely pure samples show no luminescence. This curve is not smooth, but periodic.

5. Zinc metasilicate is more luminescent than the orthosilicate.

6. Iron oxide has a deleterious effect on luminescence.

7. Dry mixing or grinding is harmful after a certain amount. Intimate mixture by means of solution is very beneficial to luminescence.

8. Luminescence increases rapidly at first with increasing time of fusion, then gradually becomes constant after about twenty-five minutes.

9. Luminescence increases rapidly but regularly, with increasing temperature of fusion, up to about 1150°C after which it remains constant.

10. Compounds similar to zinc silicate all show more or less luminescence when excited by cathode rays.

11. Blue light produces phosphorescence best of those tried, then green, then yellow.

12. Microscopic studies show that luminescent samples are semicrystalline.

13. The amount of luminescence that can be excited in samples decays rather rapidly for the first two or three days, and then gradually becomes constant.

14. Color of fluorescence is influenced by: (a) nature of sensitizing agent; (b) amount of sensitizer; (c) temperature of fusion; (d) time of fusion; (e) nature of the exciting agency; (f) atomic weight of base used.

The authors wish to express their keen appreciation to the following persons for suggestions and cooperation in carrying out this investigation: Professors Jakob Kunz and W. H. Rodebush, University of Illinois; Professor E. L. Nichols, Cornell University; Mr. W. S. Andrews, General Electric Company; and Mr. W. L. Lemcke, Franklin, Pennsylvania.

UNIVERSITY OF ILLINOIS,
URBANA, ILLINOIS,
JUNE 10, 1925.

Effect of varying field Strength on Currents in Gases.—Following a method of Townsend's, two of his pupils place a filament between and parallel to two plates, charge the plates to a potential difference V and the filament to the potential of the equipotential plane in which it lies, and measure the currents between the two plates and the filament as functions of V. They increase rather rapidly with the voltage and (therefore) with the field strength. The distance between the plates is then increased and the potential between them correspondingly increased, so as to study the effect of a change in the total P.D. across the chamber without a correlated change in field strength. It is then found that over a rather wide range in voltage the currents are unaffected, so that the originally observed dependence of the currents on V is due to an effect of field strength. The experiment may thus be considered as a source of information about the dependence of ionization on field strength in a gas traversed by electrons.—[S. P. McCollum and C. M. Focken, Oxford; Phil. Mag., *49*, pp. 1309-1320; 1925].

KARL K. DARROW

Hyper-fine-structure.—After having arranged spectrum-lines into series, and then divided each line into components, we now have to go a step further and subdivide each component into sub-components. This means that having become accustomed to a threefold classification of stationary states with three quantum numbers, we must now prepare to see it enlarged into a fourfold classification with four quantum numbers. The first steps in this direction have been taken by Ruark and by Joos, the latter of whom analyzes the "hyper-fine structure" of the three lines of the Cd triplet $2p_1-2s$, $2p_2-2s$ and $2p_3-2s$, and lays down a system of stationary states which would account for them. Some of the transitions between these stationary states do not correspond to observed lines, and it is possible so to assign values of a new quantum number to them that transitions take place only between

levels for which the new quantum number differs by ± 1 or 0, and the transition $0 \rightarrow 0$ is excluded. The Bi line $\lambda 4722$ has 6 components which can be correlated with transitions between 3 initial and 3 final states, with a similar rule of selection.—[G. Joos, Phys. ZS., *26*, pp. 380-382; 1925.]

KARL K. DARROW

Enduring Electrical Polarization of Certain Dielectrics.—Plates of certain dielectric substances (e.g., certain samples of glass, paraffin properly pretreated, wax, stearin, etc.), when exposed to a transverse electric field of the order of several thousand volts/cm, develop a polarization in the normal direction which lasts 10-30 minutes after the field is withdrawn. Others (e.g., ebonite, sulphur, mica), develop a polarization in the opposite sense (positive side of the plate towards the positive electrode), which may last for months. A test plate applied to the polarized plate, earthed, connected to an electrometer and lifted off the plate, may cause an electrometer deflection amounting to tens of thousands of volts. The first phenomenon is ascribed by the author to migration of ions within the plates, especially since it is shown by substances which are bad conductors but not first-rate insulators; the second is attributed to adhesion of ions from the air to the surfaces of the plate while it lies temporarily polarized between the charged electrodes and this idea is based on the fact that it is displayed especially by good insulators which are hygroscopic in moist air. The polarization of a plate may change in sign from the first type to the second some minutes after the field is removed, presumably because the two effects co-existed and the first decayed sooner. This sounds somewhat like the account of Eguchi's "electret" (cf. This JOURNAL, *11*, p. 66; 1925).—[S. Mikola, Budapest; ZS. f. Phys., *32*, pp. 476-488; 1925.]

KARL K. DARROW

Variation with Temperature of the Reflection of X-rays from Quartz.—This article consists essentially of a few curves of reflected intensity vs. temperature, for a single incident wave length and three different sets of atom planes; the only feature emphasized is that most of them display curious bends, cusps, or wiggles more or less in the neighborhood of 575° C. where quartz suffers a transition. The experimental conditions do not seem to have been remarkably good, and apparently it is tacitly assumed that changes in temperature have no effect on the intensity of reflection except insofar as they affect the atom lattice, which is strange.—[R. E. Gibbs, University College; Proc. Roy. Soc. A,*107*, pp. 561-570, 1925.]

KARL K. DARROW

INSTRUMENT SECTION

THE HYDRO-OSCILLOSCOPE

By Vladimir Rojansky

The comparison of an electric current to a flow of water is indeed one of the most useful comparisons a teacher of elementary electricity can make in a classroom. The analogy appeals to one's imagination and since the most fundamental laws of direct currents correspond to the laws of flow of liquids it is widely used. In the study of alternating currents, however, the water-flow analogy is usually abandoned, and to clarify by mechanical analogy the action of resistance, inductance, and capacity, separate illustrations involving friction, inertia, and elasticity are usually drawn.

The illustrative value of the water-flow analogy is indeed great, and the appreciation of this value led to the construction of the apparatus briefly described below. "Hydro-oscilloscope" is the name which the writer associates with this apparatus, which is devised to illustrate in the classroom and in the laboratory some of the fundamental relations between the variables involved in the fundamental equations pertaining to alternating electric currents:

$$L\frac{d^2i}{dt^2}+R\frac{di}{dt}+\frac{i}{C}=\frac{de}{dt};$$

$$\tan\theta=\frac{\omega L-\dfrac{1}{\omega C}}{R};$$

$$\text{watts}=EI\cos\theta\,.$$

It is to be understood that the writer's aim was to construct a machine that may be of practical use in instruction and that therefore he did not hesitate to make several approximations that allow considerable simplifications of the apparatus. It seems to the writer that the idea of a flow is so valuable in any analogy of an alternating current that retaining it justifies the necessary approximations.

The hydro-oscilloscope is represented diagrammatically in Fig. 1. It consists essentially of four vertical vessels A, K, K', and A' connected by the tubes T, T', and P, and two heavy plungers W and W' which

can be made to oscillate vertically in A and A'. The vessels are filled with a liquid so that with W and W' in their middle position the levels in all four vessels are at NN'. The pet-cock in P is opened while the vessels are being filled and closed after the levels had equalized. Other parts of the apparatus shown in the diagram are for transmitting motion to the plungers and for recording the angle of phase difference. They will not be referred to while the fundamental equation of flow is derived, and the presence of the part V is to be temporarily disregarded.

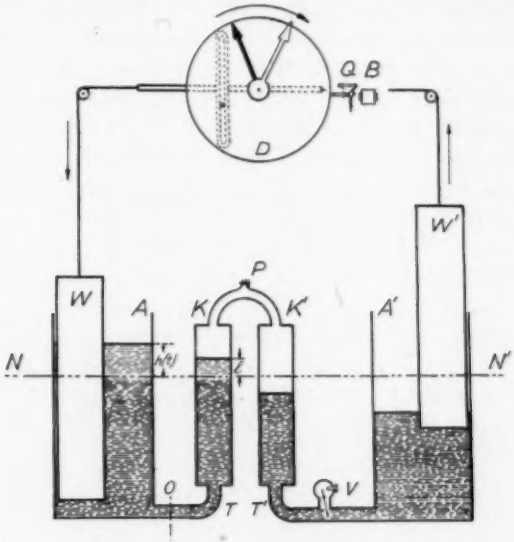

FIG. 1. *Diagram of the hydro-oscilloscope.*

The horizontal cross sections of A and A' are assumed to be great in comparison with the horizontal cross sections of K and K' which are equal and are denoted by S. S is in turn great if compared with the cross section of T and T', denoted by a. While the apparatus is in action the motion of the plungers W and W' is kept slow, so that the velocity of flow in T and T' is small enough to justify neglecting that part of friction in the tubes which is proportional to the square of velocity.

In order to derive the equation of flow of the liquid in the apparatus due to the oscillations of the plungers it is assumed that at any time t the displacement of the levels in A and A' in respect to NN' is equal to $h(t)$ and is in opposite directions in the two vessels. Due to the difference of levels in A and A' there is a force acting across any section

of the circuit, and across the section O (say) of T this force is equal to $2a\delta h(t)$, where δ is the density of the liquid.

If the velocity of flow through the section O be denoted by v the height of the level in K above the line NN' is at any moment equal to

$$l = \frac{a\int v dt}{S}$$

This head supplies one of the three forces balancing the force due to the disturbance of levels in A and A'. The sizes of the vessels being as described above and the velocity of flow through T being very small, it may be safely assumed that the retarding force due to the inertia of the liquid is equal to $M\,dv/dt$, where M does not depend on velocity but upon the dimensions of the apparatus and the density of the liquid employed. The third force is the frictional resistance and is equal to Fv, nearly.

The equation of flow can now be obtained by equating the forces:

$$M\frac{dv}{dt} + Fv + \frac{2a^2\delta}{S}\int v dt = 2a\delta h(t)$$

Differentiated in respect to t this equation gives:

$$M\frac{d^2v}{dt^2} + F\frac{dv}{dt} + \frac{2a^2\delta}{S}v = 2a\delta\frac{dh}{dt}$$

which by the substitutions:

$$L' = M\ ,\ R' = F\ ,\ C' = \frac{S}{2a^2\delta} \text{ and } e' = 2a\delta h$$

is transformed into an equation equivalent to the equation of an alternating current:

$$L'\frac{d^2v}{dt^2} + R'\frac{dv}{dt} + \frac{v}{C'} = \frac{de'}{dt}$$

This equation shows that if the head be regarded as "impressed emf," the inertia of the liquid in the connecting tubes as "inductance," frictional resistance of the tubes as "ohmic resistance" and the volume capacity per unit height of the vessels K and K' as "electric capacity" then the velocity of flow varies just as an electric current does under similar conditions. These are the familiar analogies to the electric quantities: force, inertia, friction, and elasticity.

In order to demonstrate the dependence of the phase of the current upon the constants of the circuit and upon the frequency of the im-

pressed emf the apparatus is provided with a disc D and two arrows: one, recording the relative position of the levels in A and A', and the other controlled by the flow in the tubes. Fig. 1 shows that the plungers W and W' are executing sine oscillations, the position of the plungers and therefore of the levels in A and A' being dependent upon the position of the disc D, which is rotated slowly by a motor. Connected fast to the disc there is an arrow (shown as black in the drawing), which is so placed that at the moment when it points horizontally to the right the plungers are in their middle position, so that if there were no phase difference between the oscillations of the levels and the oscillations of the velocity of flow, the velocity would be equal to zero at that moment. Thus, the projection of the black arrow upon the vertical axis of the disc represents very nearly in magnitude and sign the value of the "impressed emf" at any moment.

To record the phase of the "current," that is, the phase of the velocity, the disc D is provided with the second arrow, shown as white. This arrow is not rigidly fastened to the disc, but is held by friction, so that it rotates with the disc only if nothing from the outside is in its way. If, however, its way be obstructed, it remains still until released.

To make the angle between the two arrows equal to the phase difference between the "impressed emf" and the "current" there is a small vane placed in the chamber V. Oscillating according to the actual flow of the liquid (water) in the tubes, the vane makes and breaks an electric contact once each cycle, at the moments when the velocity of flow reaches zero. This contact is in series with an electromagnet B operating a trip Q, which has two pins projecting toward the disc D. When the contact is broken by the vane the lower pin is close to the disc D and in the way of the white arrow. When the contact is made the upper pin moves toward the disc and remains in the way of the arrow while the lower pin is drawn away by the electromagnet. Thus the electromagnet can release the arrow only at the moment when the velocity of flow passes through zero and changes its sign in a definite sense, and, therefore, the white arrow is automatically placed in such a position in respect to the black one, that the angle between the two is equal in magnitude and sign to the angle of phase difference between the "impressed emf" and the "current." Once thus placed the white arrow remains in the same position in respect to the black one until some of the constants of the circuit or the frequency are changed, when the arrow is automatically shifted to a new position.

Fig. 2 shows the model of the apparatus built for experimentation, and the short table below gives an idea as to the variations of the angle of phase difference obtainable. On the model some of the parts are not in the best relative position and some lack considerably in mechanical precision. The values of θ are, however, consistent in spite of the fact that $h(t)$ is only a rough approximation to a sine function and regardless

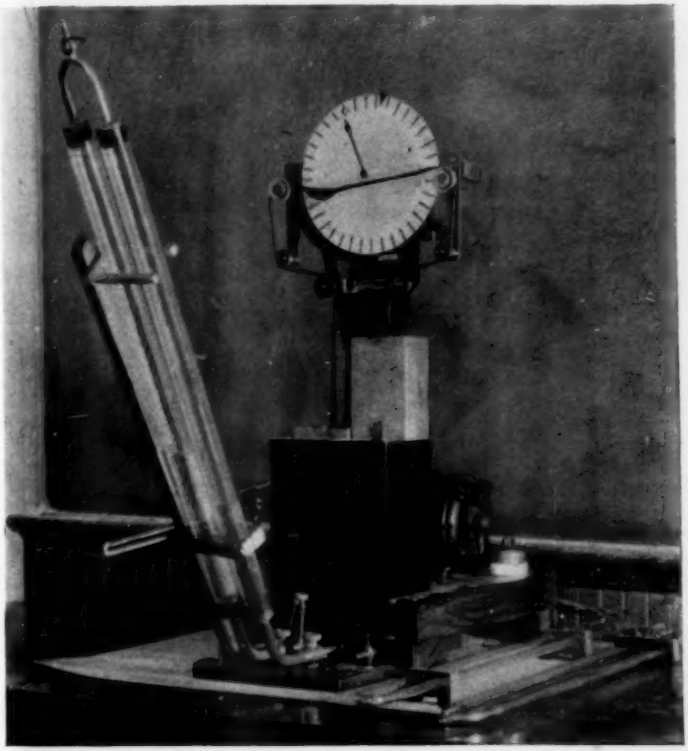

FIG. 2. *Trial model of the hydro-oscilloscope.*

of other defects of construction. It is to be noted that while clockwise rotation of the disc D was adopted in the model and, therefore, in this article, anti-clockwise rotation of the arrows, more convenient in vectorial representation of currents, may be obtained by a slight rearrangement of parts.

In this model the frequency is varied by shifting the belt from one set of pulleys to another, there being three steps. The "inductance" is

varied by inserting different lengths of tubing for T and T'. The photograph shows one of the U-shaped "inductances" lying by the side of the machine. It was suggested to the writer by Mr. E. J. Workman that the "inductance" tubes might be constructed in a "trombone" fashion to allow changes in "inductance" of the circuit to be made without taking out any parts of the tubing.

"Capacity," as was shown, depends upon the horizontal cross section of the vessels K and K' and may, therefore, be varied by inserting different sets of vessels into the circuit. It is possible, however, to vary the horizontal cross section of K and K' by tilting the vessels and thus increasing their horizontal cross section, the air pressure being each time brought to that of the atmosphere by opening for a moment the petcock in P. Fig. 2 shows a circuit with a large "condenser" tilted at 30° to the vertical, the "capacity" of it being C sec 30° where C is its "capacity" when vertical. A smaller "condenser" is shown by the side of the "inductance" on the table. The "resistance" can be varied by closing somewhat the stop-cocks in T and T', but only within narrow limits on account of the turbulent flow thus caused.

TABLE 1. *Values of the angle of phase difference.*

"Resistance"		stop-cocks fully open						partly closed
"Inductance"		tubes 33 cm long				193 cm long		
"Capacity"		C	1.2C	1.4C	2.0C	no "condenser"		
"Frequency"	6.7 RPM	+52°	+47°	+35°	+30°	−10°	−45°	−30°
	15 RPM	0°	− 3°	−15°	−20°	−35°	−80°	−63°

The values quoted in this table were obtained with the arrangement shown in Fig. 2. The "capacity" of the large "condenser" when it is vertical is denoted by C. Positive angles denote lead, negative—lag.

The machine is driven by a 1/12 H.P., 110-volt induction motor. The inductance of the electromagnet B is made great enough to allow impression of 110 volts on the circuit controlled by the vane, and therefore one cord connected to a 110-volt A.C. main supplies the current for both the motor and the electromagnetic trip. The electromagnet is placed behind the disc and in Fig. 2 can be partly seen behind the upper right pulley. The arrow shown in white in the diagram is also behind the disc, its pointer bent over and seen from in front. In the photograph the machine registers a lead of the "current" ahead of the

"impressed emf" equal to 35°. If both arrows be completely seen from in front the apparatus may serve to derive in a very elementary way the formula—watts $= EI\cos\theta$ by showing what part of the power is only apparently consumed during a cycle.

The way in which the levels are oscillated in the model is open to several objections. An arrangement which seems to the writer to be best suited to the aims of the apparatus is that suggested by Dr. W. E. Milne and shown in Fig. 3. This construction eliminates the awkward plungers, makes the oscillations as nearly sinusoidal as necessary and brings out very clearly the oscillation of the levels that is the cause of the alternating flow.

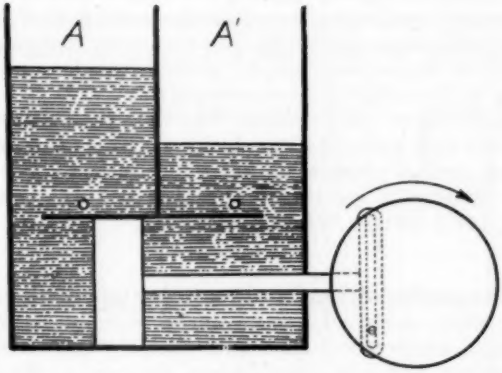

FIG. 3. *A suggested arrangement for oscillating the levels.*

It is a great pleasure for the writer to express his thanks to Professor B. H. Brown of Whitman College for the initial stimulus given to the work and helpful advice, to Mr. E. J. Workman, Instructor of Physics in Whitman College, for collaboration and the construction of the first working model of the apparatus in which oscillations of the levels were effected by oscillating the vessels A and A', and to Dr. W. P. Boynton who placed at the writer's disposal the facilities of the Physics Laboratory of the University of Oregon, where the present model was built.

UNIVERSITY OF OREGON,
EUGENE, OREGON,
JUNE 2, 1925.

Spectra of solid Nitrogen, pure and mixed with Neon at 4° K.—The spectra are produced by bombardment with fast electrons, and for pure nitrogen consist of a number of bands, of which one lies in the green with its maximum at 5555A, about 22A below the wave length of the auroral green line. When neon is mixed with the nitrogen, the position of this band is unaffected until the percentage of Ne surpasses 70, after which it glides over to and slightly past the value (5577.35) of wave length for the auroral green line. The authors seem to think that the auroral green line is due to impacts of fast electrons on particles of solid nitrogen contaminated with just the right proportion of neon.—[L. Vegard, H. K. Onnes, and W. H. Keesom; C.R., *180*, pp. 1084-1087, 1925.]

KARL K. DARROW

Equality of initial Speeds among the Alpha-rays of Polonium.—Experiments by applying a transverse magnetic field of 10000 gauss to a beam of alpha-rays limited by two extremely narrow (0.05 mm) slits and received upon a photographic plate revealed no trace of such a spreading out of the deflected beam as would result from non-uniformity of the initial speeds of the particles. The data are believed accurate enough to prove that if the speeds are really distributed according to the error-function about a mean value, three fourths of the particles must have speeds differing by less than 0.3 per cent from the mean speed.—[Irene Curie, C.R., *180*, pp. 831-833; 1925.]

KARL K. DARROW

Curious Properties of bent and restraightened nickel Wire.—Nickel wire, when stretched, ceases almost entirely to produce the clicks and other noises which are heard when the unstretched wire is slowly magnetized, and which Barkhausen discovered. When the wire is bent into a circular arc of 4.5 mm radius and restraightened, the clicks reappear. These processes also alter the hysteresis loop, which after stretching becomes very thin and narrow, and after bending and restraightening becomes wide and fat, with larger discontinuities. These discontinuities are, in fact, so large that sometimes an increase in the magnetizing current produces an actual decrease in the magnetizing field within the metal, owing to the demagnetizing factor.—[R. Forrer, C.R., *180*, pp. 1253-1255, 1925.]

KARL K. DARROW

Radiations emanating from a poor Conductor traversed by an electric Current.—These radiations, which are detected and measured by their ionizing effect in air or some other gas, are absorbed in gases to an extent which suggests that they are extremely inhomogeneous and their wave lengths are of the order of magnitude of a few tens to a few hundreds of Angstroms.—[G. Reboul; C.R., *180*, pp. 916-919; 1925.]

KARL K. DARROW

CAPACITY MEASUREMENT WITH A DOUBLE OSCILLATOR

By A. L. Fitch

The measurement of capacities at high frequencies is complicated in some cases by the necessity of supplying some special indicating device for these frequencies. This difficulty is eliminated by the method shown diagrammatically in Fig. 1.

Two Hartley oscillators operate on the same plate battery and through the same receivers. The note given by the receivers will then be a beat note and therefore the frequencies used may be far above the audible range without in any way destroying the usefullness of the circuit.

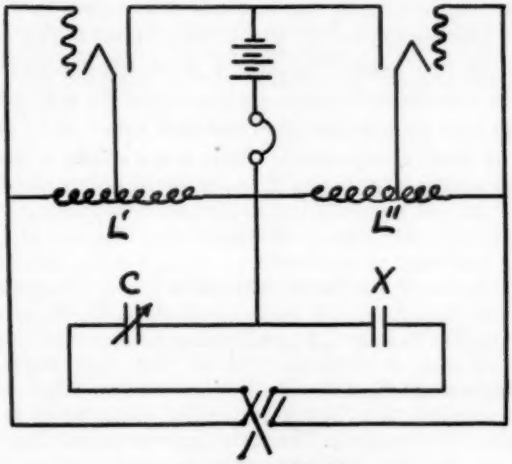

Fig. 1. *The double oscillator.*

Two vacuum tubes of the same type are chosen. The filaments are lighted from separate batteries. Two inductances are chosen that are nearly of the same value; it is desirable that one of the inductances be variable over a range which includes the value of the other. A calibrated condenser continuously variable over the range that will include the capacity of the unknown is placed at *C*. The unknown is placed at *X*. The frequencies produced by the two oscillators will in general be

different but may be made the same by varying C until the beat note vanishes. The frequencies of the two oscillators being equal

$$(C'+\delta')L'=(X+\delta'')L''$$

where C' is written for the capacity of C for this setting and L', L'' and X are as indicated while δ' and δ'' are the distributed capacities of the circuits and tubes. The switch is then thrown down, interchanging C and X. A new setting of C will be necessary in order to eliminate the beat note unless L' and L'' are alike in value. Call the new setting C''. Then

$$(C''+\delta'')L''=(X+\delta')L'$$

If the δ's are negligible

$$X=\sqrt{C'C''}$$

If the δ's are not negligible the variable inductance may be used to advantage. The readings of C' and C'' are taken as described above. If these are not very nearly the same, C is adjusted to an intermediate value and the variable inductance adjusted until the beat note vanishes. The readings may then be repeated and new values of C' and C'' read which will be more nearly equal. After a few trials, a condition will ordinarily be attained where

$$C'=C''$$

Then

$$(C'+\delta')L'=(X+\delta'')L''$$

and

$$(C'+\delta'')L''=(X+\delta')L'$$

These equations result in

$$\frac{C'+\delta'}{X+\delta'}=\frac{X+\delta''}{C'+\delta''}$$

which manifestly can hold only when

$$X=C'$$

The following readings were taken on two variable air condensers of the same type and nominal capacities with maximum values at setting 100 divisions of 0.001 mf. The inductances used were a coil of nominal value 0.25 henry and a Leeds & Northrup variable inductance

with maximum value 0.25 henry. The variable inductance read 0.247 henry during the taking of data.

C	X
92.5 div	100 div.
84	90
74.5	80
66	70
57	60

The note produced by the oscillators was inaudible for settings of the condensers below 85 divisions.

UNIVERSITY OF MAINE,
ORONO, MAINE.

Gas discharge Tube showing the Spectra of Mercury and Neon Side by Side.—A tube consisting of a series of wide sections alternating with narrow sections, containing neon at a pressure suitable for the glow discharge and mercury vapor as well, shines with the characteristic color and spectrum of excited neon in the narrow sections and of excited mercury in the wide ones. This is attributed by the author to the different current densities in the alternating sections.—[G. Claude, C.R., *180*, pp. 890-892; 1925.]

KARL K. DARROW

Recoil-electrons involved in X-ray Scattering.—Like C. T. R. Wilson, Compton, and Simon, Ikeuti observes the tracks of electrons produced in air by high-frequency x-rays (the *K*-rays of tungsten, $\lambda = 0.21$A) and finds it easy to discriminate between the long trails (averaging some 7.5 cm) of photoelectrons and the short trails (less than 0.4 mm) of recoiling electrons from which quanta have presumably rebounded in the manner prescribed by Compton's theory. The lengths of these short trails, and the relation between their lengths and their directions, agree rather well with Compton's theory; the ratio of the number of short trails to the number of long trails agrees quite well with the ratio of scattering coefficient to absorption coefficient for the x-rays; however, there are some definite, though not very violent oppositions between theory and experiment. [H. Ikeuti, C. R., *180*, pp. 1257-1259; 1925.]

KARL K. DARROW

Broadening of spectrum Lines.—There is a close correlation between: (*a*) broadening of lines in the spectrum of an arc when the current density is very great; (*b*) broadening of lines in the spectrum of an "interrupted" arc, or break-arc; (*c*) displacement and resolution of lines when a strong electric field is applied to the radiating atoms (Stark effect). The implication is that the effect is produced in all cases by strong electric fields, varying rapidly in direction and magnitude in cases (*a*) and (*b*), constant and controllable in (*c*). Lowery's data relate to broadening of lines of Ag, Au, Cu, Ni, and Fe, produced in the second fashion; the observations on broadening produced in the first way are by Kimura and Nakamura.—[H. Lowery, Manchester; Phil. Mag., *49*, pp. 1176-1183; 1925].

KARL K. DARROW

First Measurements of the K emission Frequencies of some massive Atoms.—Measurements given to five significant figures of the α_1, α_2, β and γ frequencies of the *K*-series of the elements Ta, W, Os, Ir, Pt, Au, Tl, Pb, and U; these are stated to be unprecedented except for Au and Pt. The *K* frequency of uranium, which must be the highest emission frequency yet observed except for rays proceeding from nuclei, corresponds to λ 108.42X.—[G. Rechou, C.R., *180*, pp. 1107-1108; 1925.]

KARL K. DARROW

AN ALTERNATING CURRENT BRIDGE FOR MEASURING SMALL PHASE ANGLES IN HIGH RESISTANCES

By Irving Wolff

ABSTRACT

An alternating current bridge is described which may be used for measuring large capacities in series with high resistances or small phase angles in high resistance boxes. Using this bridge it is possible to compensate for the capacity and inductive effects in the standard resistance boxes and in the arms of the bridge. This correction is effected by the method developed for the adjustment of the Wagner earthing arm. Circuit equations are given to show the extent to which errors are eliminated, and experimental results in some typical cases are shown.

The measurement of pure capacities of the order of one microfarad by alternating current bridge methods can be carried out to a high degree of precision. If however, 1 microfarad is in series with a resistance of more than 10 000 ohms, strict precautions must be taken in order to get a value which is correct to even a few per cent.[1] The difficulties encountered in these measurements are of two kinds. In the first place, since the impedance of 1 microfarad at 1000 cycles per second is only 160 ohms it is obvious that a sensitive detecting instrument must be used in order to measure this capacity to 1 per cent. A more serious difficulty arises due to the fact that the best resistance boxes will usually have enough distributed capacity or inductance to spoil the measurement.

The development of the vacuum tube amplifier has made possible a detector of the required sensitiveness, and when proper precautions are taken its use in a bridge is very satisfactory. For most purposes good results are obtained by thoroughly shielding the detector in a grounded iron case and adding the so called Wagner earthing arm to the bridge.[2] It is also an advantage to introduce electrostatic shielding between the primary and secondary of the transformer connecting bridge and amplifier.

It is usual to fix the resistances in this extra arm so that the detector shall be at earth potential. In this article a method is described whose action depends on having the Wagner arms so adjusted that the detector shall be somewhat away from earth potential. In order to get satisfactory results with this method it is necessary to eliminate the screening

[1] K. F. Sun, Phys. Rev., *23*, p. 617; 1923.
[2] K. W. Wagner, Electotech, Zeit., *32*, p. 100; 1911.

between the windings of the transformer connecting the bridge and detector.

Referring to Fig. 1 let us suppose that the arms R_1, R_2, R_3, R_4, are so adjusted that the resistances are all equal and therefore that the bridge is arithmetically balanced. Let us suppose that R_5 is slightly greater than R_6. Some point on each of the bridge arms R_2 and R_4 will then be at an earth potential and the points c and d will be at some small alternating potential. The transformer T has the filament side of its

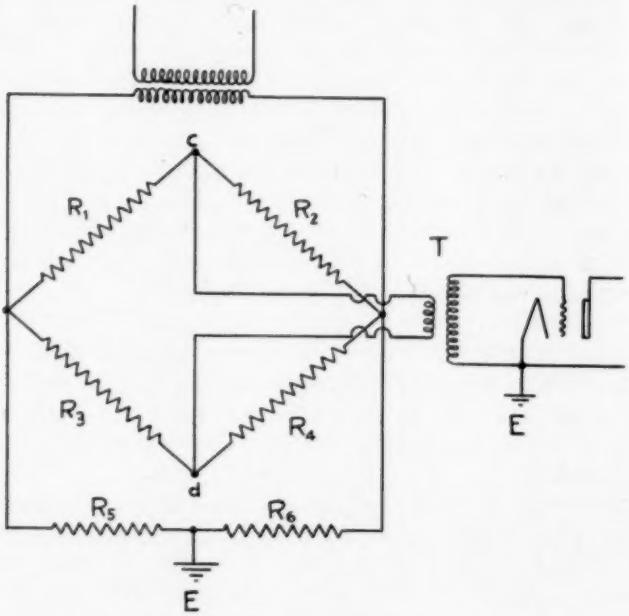

FIG. 1. *Standard bridge with Wagner arm and amplifier*

secondary grounded as shown. Since the primary and secondary windings of the transformer will act as the plates of a condenser, an additional high impedance circuit will thus be created from E through the bridge and T and then back to E. An alternating potential will then be given to the grid of the first tube of the amplifier for two reasons. 1) In general the currents in the primary side of T will not divide so as to induce equal and opposite emfs in the secondary. 2) Currents flowing from earth to the secondary of T will on account of the high inductive impedance of the secondary impose an alternating potential on the grid. We have

thus a method for introducing an emf of small magnitude on the detector. The phase of this potential with respect to that applied to the bridge will depend on the bridge and the transformer characteristics. It may be shifted by placing a combination of resistance and capacity in the Wagner arms instead of pure resistances.

If there is no reason for suspecting any error in the bridge this extra emf applied to the tube should be reduced to zero. The preceding analysis shows that this can be readily accomplished by keeping c and d at ground potential and by interposing an electrostatic shield between the primary and secondary of the transformer as described above. This is the usual method of adjusting the Wagner arms.[3]

It is well known, however, that there are other effects inherent in the bridge arms which may cause serious error when an attempt is made to measure small phase angles of high resistances. By having the Wagner arms unbalanced by the correct amount it should be possible to introduce an emf which will just balance that due to these errors. A method will now be described for making this adjustment. The circuit diagrams are shown in Figs. 2, 3, and 4 which differ from each other only in the opening or closing of certain switches.

Suppose that it is necessary to measure the combination R_xC_x composed of a non-inductive resistance R_x in series with a pure capacity C_x. The Wien bridge, in which the capacity is balanced with a variable inductance in the same arm will be used to illustrate the manipulation. The bridge could be easily modified so as to be used with other well known methods of capacity measurement.

The coils R_1 R_2 used in this bridge must be balanced as regards resistance and phase angle. R_3' and R_4' should be small phase angle resistance boxes ranging to 1000 ohms, and R_3 is a resistance box of the same order of resistance as the unknown. L is a variable inductance of the correct order of magnitude to balance C_x.

The first setting is shown in Fig. 2 The object of this setting is to measure the resistance R_x. As it is carried through in the usual manner no further description is necessary here. After the resistance R_3 is set for this measurement it must remain unchanged for the remainder of the adjustments. Setting No. 2 obtained by adjusting R_5 and R_4' is shown in Fig. 3 and adjusts the Wagner arms so as to eliminate the capacity or inductance effects in the resistance boxes, earth capacity effects in the arms of the bridge, and slight errors that might be present due to imperfect shielding of the amplifier. A detailed analysis is given

[3] K. W. Wagner, *loc. cit.*

FIG. 2. *Setting 1. Bridge for measuring small phase angles*

FIG. 3. *Setting 2. Bridge for measuring small phase angles*

FIG. 4. *Setting 3. Bridge for measuring small phase angles*

below. Setting No. 3 made by adjusting R_4' and L, is shown in Fig. 4, and completes the measurement by determining the unknown capacity.

Referring now to setting 2 it is evident that in general it will not be possible to balance the bridge as shown while R_5 equals R_6. It is then best to fix R_3' at some convenient value, say 900 ohms and vary R_4' and R_5 until silence is secured in the phones. Although it is possible to solve the network completely for the condition of this balance it will not be done here, as certain approximations which may be made, allow the analysis to be much simplified. The emf applied to the detector tube will be divided into three parts. E_b due to the adjustment of the bridge arms, E_w due to adjustment of the Wagner arms and E_s caused by imperfect shielding of the amplifier. For silence $E_b+E_w+E_s=0$. Since the success of the bridge depends on this fact, it is important to note here that E_w will be unchanged so long as R_5 and R_6 remain fixed and the total impedance of each of the bridge arms is constant. In shifting from setting 2 to setting 3 all the changes are made in arm 4. Neglecting for the moment the earth capacity effects in this arm, it is obvious that the impedance and phase angle of the arm must remain constant during the change, i.e., since E_w and E_s remain constant, E_b must do so also. Suppose that the impedance of box R_4' expressed in symbolic notation is r_4+jq_4 in setting 2, and $r_4'+jq_4'$ in setting 3. Let us find what kind of an impedance must be added in arm X in setting 3 in order to keep the bridge balanced. Call the impedance r_x+jq_x. The above considerations show that

$$\frac{1}{r_4+jq_4}=\frac{1}{r_4'+jq_4'}+\frac{1}{r_x+jq_x}$$

Separating real and imaginary parts, the imaginary part of the equation may be put in the following form

$$q_x=\left\{\frac{q_4}{r_4^2+q_4^2}-\frac{q_4'}{(r_4')^2+(q_4')^2}\right\}\left\{r_x^2+q_x^2\right\}$$

writing instead of r_4' and q_4', r_4+R and q_4+Q, and neglecting q_4 and R in comparison with r_4, Q in comparison with q_4, and q_x in comparison with r_x

$$q_x=\frac{2r_x^2Rq_4}{r_4^3}-\frac{r_x^2Q}{r_4^2}$$

Since $\dfrac{1}{r_4+R}+\dfrac{1}{r_x}=\dfrac{1}{r_4}$ very nearly, we get, again neglecting R in comparison with r_4, $r_4^2=Rr_x$ and

$$q_x=2r_x\left(\frac{q_4}{r_4}\right)-r_x\left(\frac{Q}{R}\right)$$

$\frac{q_4}{r_4}$ is the phase angle of box R_4' in setting 2, while $\frac{Q}{R}$ is the phase angle of the resistance added between settings 2 and 3.

In order to make the measurement of capacity accurately the balance should occur when the capacity is just balanced by the inductance, i.e., $L=1/C\omega^2$ where ω is 2π times the frequency. The above arithmetic shows that the inductance required is increased by a certain amount q_x/ω. In order to determine the effectiveness of the method it is necessary to estimate the magnitude of this quantity and adjust the bridge so that it is a minimum. It is obvious that this error is a minimum when the phase angle of box R_4' is a minimum. It should be remembered at the same time that increasing the resistance in box R_4' increases the sensitiveness of the setting. The author has found that a resistance of about 900 ohms wound by the Ayrton method gives both satisfactory sensitiveness and phase angle. This is shown in tests made and tabulated in table 1. The resistance used in the box R_4' in these tests was always between 500 and 900 ohms.

Equation (1) also shows that the final setting is independent of any capacity or inductive effects in the high resistance box R_3'.

The elimination of earth capacity effects is not quite so complete but an estimate of their value may be made in the following manner. Make the setting first as shown in the diagram and note the inductance. Go through the setting completely again, this time with the switch open at the outside end of arm R_4' in setting 2. In the first setting the Wagner arm was adjusted so as to eliminate the earth capacity of the unknown when it was entirely at the high potential of the bridge, while in the second setting it is almost at earth potential. In the final setting parts of the unknown lie between these two potentials and the capacity to earth which should have been eliminated will lie between these amounts. In the measurements taken by the author the difference between the two settings was usually small enough to be neglected.

In the table the results of some measurements of capacity by this method are compared with the same measurements taken when the Wagner arms are adjusted in the usual manner. In the first column are shown the coils used in R_3' in order to get balance. These are coils in high grade small phase angle resistance boxes chosen at random. It will be noted that changing the coils makes practically no difference in the capacity as measured by this method. The last column which shows the measurement made in the usual manner indicates that a considerable distributed capacity or inductance actually existed in the coils

used for balancing and that the concordant results in column 2 are due to the elimination of its effect.

TABLE

Capacity C_x mf	Frequency cycles/sec	Series resistance R_x Ω	Coils used in box R_3	Measured capacity	Mf
				Adjustment of Wagner arms as described	Standard adjustment
.98	1100	40,000	1−40,000Ω	.95	.89
.98	1100	40,000	1−30,000Ω +10-1000Ω	.97	1.42
.202	3000	1,000	1−1000Ω+	....	.202
.202	3000	20,000	1−20,000Ω	.198	.196
.202	3000	20,000	1−10,000Ω+ +10-1000Ω	.200	.163

In conclusion I wish to express my appreciation to Professor C. C. Murdock for his aid in securing necessary apparatus and for his helpful suggestions and criticisms.

PHYSICAL LABORATORY,
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ITHACA, NEW YORK.

Absorption Spectra of Indium and Thallium.—A study of the absorption spectra of these metals in the vapor state, made over a wave length range from 6000 to 2000A, again confirms the well established fact that the normal state of the atom of each of these elements, as of Al, is a p_2 state instead of an s state. The sharp and diffuse series both appear in the absorption spectra, the latter very strongly, but the principal series does not appear at all. Transitions from any initial level into the first p_2 state appear to be much more abundant than transitions into the p_1 state from the same level.—[M. K. Rao, Madras; Proc. Phys. Soc. London, *37*, pp. 259-264; 1925.]

KARL K. DARROW

Arrangement of Molecules in thin Films of organic Acids.—Thin films produced by dissolving fatty acids in alcohol, pouring a few drops on a clean sheet of glass, and letting them evaporate, diffract x-rays quite intensely in the manner of a series of parallel layers; lines in all orders up to the seventh are photographed with three-fourths hour of exposure, and lines can be detected with absolutely invisible films 1μ thick. Measurements on a series of fatty acids with molecules just alike except that they include 8, 10, 12, 14, 16, and 18 carbon atoms, respectively, show that the spacing between layers increases by (3.95 ± 0.05)A for each additional pair of carbon atoms. Measurements on a series of acids of the composition $CO_2H-(CH_2)_n-CO_2H$ with $n=2$, 4, 6, 8, show that each pair of CH_2 groups adds roughly 2.3A to the spacing; the acids of the same type with $n=5$, 7 do not lie midway between those with $n=4$, 6 and $n=6$, 8 respectively, but eccentrically.—[J. J. Trillat, C. R., *180*, pp. 1329-1332; 1925.]

KARL K. DARROW

A RAPID AND ACCURATE METHOD OF CORRECTING MEASUREMENTS WITH EMANATION ELECTROSCOPES FOR ORDINARY CHANGES IN TEMPERATURE AND PRESSURE

By O. C. Lester

ABSTRACT

Errors due to these variations are usually neglected though they may amount to three or four per cent in measurements claimed to be accurate to within one per cent. Assuming that an electroscope has been standardized at a given pressure and temperature, it is shown that the necessary calculations can be made once for all. From these calculations a chart is constructed by means of which the constant of the electroscope, corresponding to other values of the temperature and pressure, can be obtained graphically by a single reading.

In measuring radioactivity by the emanation method, it is usual to determine first what is called the "constant" of the instrument. This constant is defined as the fraction of a curie which will produce a motion of the leaf of one division per minute or second across the eyepiece scale of the reading instrument. But this "constant" is not really a constant unless the density of the gas in the ionization chamber remains the same. The "constant" varies inversely as the ionization. The ionization varies directly as the density of the gas. The density of the gas varies directly as the pressure and inversely as the absolute temperature. Hence, we may write

$$C = K\,T/P \qquad (1)$$

Where C is the constant of the electroscope as defined above, and K is a certain other constant, the same for all temperatures and pressures, and is known accurately when C is determined carefully at a given temperature and pressure.

In a previous paper* the author has shown that for large changes in pressure the relation between the "constant" and the pressure is given by a hyperbolic curve. This curve takes no account however of variations with temperature which amount to one per cent for a change of 3°C. The percentage change in the constant for variations in temperature alone is quite nearly linear for temperatures between 10°C and 30°C which covers the range of variation usually encountered. The percentage change in the constant due to variations in pressure alone amount to 1.3 per cent per centimeter in the neighborhood of normal pressure and to about 1.6 per cent at the average pressure which we have

* Amer. Jour. Sci., *44*, p. 225; 1917.

at Boulder, Colorado. In case the pressure and temperature changes happen to assist each other, daily variations in these quantities may easily cause an error of as much as 4 per cent in a given measurement.

So far as the writer is aware such corrections are almost universally neglected. It is true that they often operate to offset each other and the error is then not large, though appreciable. They are neglected in work for which an accuracy of one per cent is claimed and though the claim

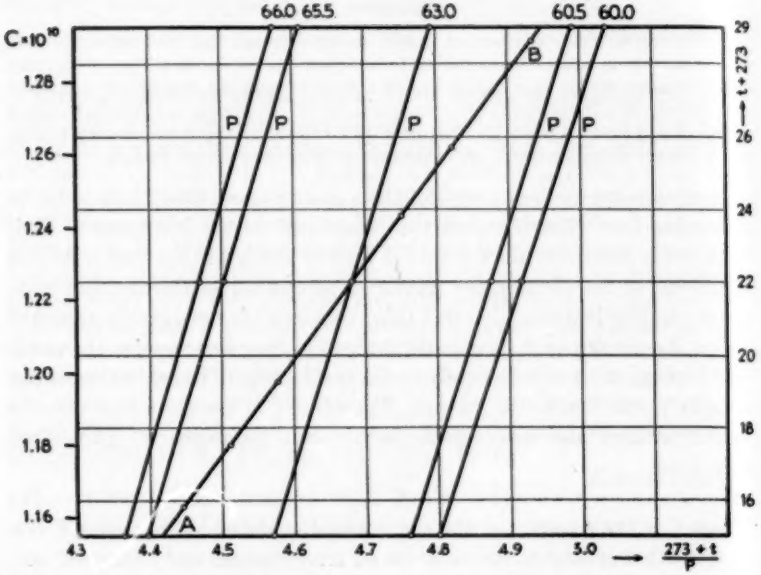

FIG. 1. *Variation of the "constant" of an electroscope with changes in pressure and temperature.*

may be sound, one is left with a doubt so long as such appreciable errors are not taken into account. The writer has found that such corrections render a series of measurements taken over some weeks or months for more concordant than they would be otherwise. This is true also for measurements with the gamma ray electroscope.

Now it is perfectly evident how these corrections should be applied, but the usual method involves no little numerical computation when many measurements are involved. The chief object of this article is to point out how a chart can be constructed once for all from which, almost at a glance and without any computation, the proper constant for any ordinary pressure and temperature can be determined graphically. All

that is needed, once the chart is constructed, is to record the barometric pressure and the temperature at the time the ionization chamber is brought to atmospheric pressure.

Let us assume that the constant of the ionization chamber has been determined accurately for a given pressure and temperature. This should be preferably the average pressure and temperature of the place although this is not necessary. Let this constant be for example $C=1.225\times10^{-10}$ curie for a pressure of 63 cm and a temperature of 22°C which are normal for Boulder. We then have data from which by means of equation (1) we can find $K=0.2616\times10^{-10}$. Hence

$$C=0.2616\times10^{-10}\ T/P \qquad (2)$$

for any other temperature and pressure. The line AB of the chart is now determined from Eq. (2) by computing a few values of C corresponding to suitably chosen values of the absolute temperature and the pressure. The pressure lines, P, $P-P$, may next be plotted by computing for each pressure, values of the ratio $\frac{273+t}{P}$ for at least three values of t covering the range of temperature expected. The values of this ratio are laid off to a suitable scale along bottom of the chart and along the top, the pressures corresponding to any line P are indicated. It is usually convenient to have a line for each half centimeter variation in pressure. The chart is completed by plotting the values of the constant along the left side of the chart and the values of $273+t$ along the right. This method of labeling the various quantities is convenient since the chart thus shows both temperature and pressure values as read on the instruments.

The non-uniformity of the variations are indicated by the pressure lines, for equal differences of pressure, being closer together on the left than on the right and by their being closer together at low than at high temperatures.

There will be a different line AB for each ionization chamber unless the construction of each is identical. The same chart may carry a number of lines like AB which is the only part of the chart based upon experimental data, each line corresponding to a different ionization chamber.

Suppose now that we have made a determination at a temperature of 20°C and at a pressure of 60.5 cm, what constant should we use? Starting on the right at the 20° line we go horizontally to the left until we hit the pressure line marked 60.5. We then go vertically until we strike the line AB, thence horizontally to the right to the constant line

where we find $C=1.267\times10^{-10}$ which is the constant to be used in reducing the reading to curies instead of the experimentally determined one, $C=1.225\times10^{-10}$.

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SIMPLIFIED LECHER WIRES FOR SHORT WAVE MEASUREMENTS

By R. R. Ramsey

ABSTRACT

A method of calibrating a wave meter for short waves, three to five meters, using an ordinary amplifying tube and a B battery. Resonance is indicated by means of a milliammeter or voltmeter in the plate circuit of the tube. Data is given showing that the accuracy of the method is better than one percent. The average deviation from the mean being about one tenth of a per cent. A simple wave meter is described.

Some years ago it was shown by Lecher and others[1] that it was possible to produce stationary electric waves on wires and that the velocity of these waves was very approximately the same as electro-magnetic waves in free space. In the early days the oscillatory discharge of a condenser through an inductance was used to produce the waves. During the last few years the three electrode tube has been used to produce the disturbance.[2] These experimenters used power tubes and rather elaborate oscillators and thermo ammeters in their work.

Recently, for student use I have adapted and devised circuits and apparatus which does not require any special apparatus more than that found in any laboratory and which gives surprisingly good results. The oscillator is the one devised by Hoffman.[3] This consists of a single turn of No. 12 copper wire four inches in diameter connected to the grid and plate terminal of an ordinary porcelain vacuum tube socket. The middle of this loop or turn of wire is cut and a .002 microfarad mica fixed condenser is inserted. Across the grid and plate terminals a special variable condenser is fastened. This condenser is made from a Cardwell condenser by removing the stator plates and substituting two plates of sheet copper. Terminals are soldered to these sheets making two variable condensers in series, the rotor being the middle of the two. The rotor is connected to the negative filament, making a Colpitts circuit. The plate current is fed to the plate through a choke coil made of 150 turns of fine wire wound in one layer on a glass tube one-fourth inch in diameter. A grid leak resistance is connected from the grid to the filament. Such an oscillator will oscillate at frequencies correspond-

[1] Fleming. The Principle of Electric Wave Telegraphy, p. 265.
[2] Townsend and Morrell, Phil. Mag., *42*, p. 265; 1921.
Huxford, Phys. Rev., *25*, p. 686; 1925.
[3] Hoffman, Q S T, p. 19; April, 1925.

ing to 3.5 meters to 5.5 meters. By reducing the capacity we have been able to get 1.8 meters with tube with base and 1.3 meters when using a tube with the base removed. A five watt tube may be used, or an ordinary 201A amplifying tube can be used with about 100 volt B battery.

The Lecher wires consist of two parallel wires fifty to one hundred feet long, strung on insulators in a hall or between two posts or trees in the open. These wires should be from ten to twenty centimeters apart and about seven feet high. At one end the wires should extend about three feet beyond the insulators. These two ends are fastened together

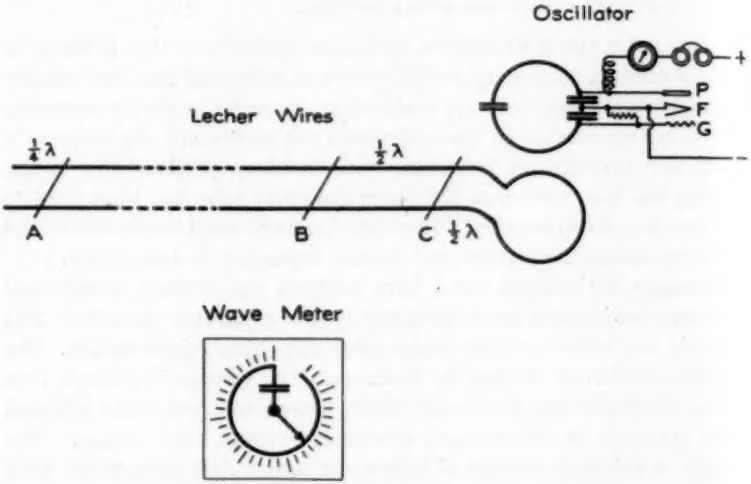

FIG. 1. *Diagram of Lecher wires, oscillator, and wave meter.*

to form a loop which can be placed near the oscillator. When using a 201A tube in the oscillator a milliammeter or voltmeter[4] used as a milliammeter is inserted in the plate circuit to indicate when the wires are in resonance with the oscillator. A head set may be substituted, using the resonance click method. When the wires and oscillator are in resonance there will be a sudden kick of the meter as the frequency of the oscillator is changed by rotating the variable condenser. If the wires are long there will be five or six such points of resonance on the dial. If the loop of the wires is too close the wires may absorb so much energy that the oscillator ceases to oscillate. Loosen the coupling so that the

[4] Ramsey, Experimental Radio, pp. 31, 98.

kick occurs at the same point on the dial when the capacity is decreasing as when the capacity is increasing.

Set the oscillator in resonance with the Lecher wires using the longest wave possible. Have an assistant connect the two Lecher wires with a short sliding wire at the far end. This will throw the Lecher wires out of resonance. Manipulate the slider until a point of resonance, A, is found. This point will be approximately one-fourth wave from the end. Then place the slider across the Lecher wires near the oscillator and find the point, C, which is one-half wave from the loop end. Then find the point, B, which is one-half wave from C. The distance $A-C$ is a whole number of half waves. $A-C/B-C$ should be near a whole number, n, say. Then A-C/n gives a better value for the length of a half wave. It will be seen that the entire length of the wires will be $n+\frac{3}{4}$ half waves. Then $(n+\frac{3}{4})\frac{1}{2}\lambda = a$ constant, L.

Find the next point of resonance and find A, B, C and L. Proceeding as above for all points of resonance, the various values of L give a check on the accuracy of the method.

The following table gives the data and results taken by one of my students. This is the data taken the first time he used the method. It will be seen that the greatest deviation from the mean is less than one per cent. From this data the oscillator can be calibrated.

Dial reading	A	B	C	$\frac{1}{2}\lambda$ approx. $C-B$	$C-A$	$n=\frac{C-A}{C-B}$	$\frac{\frac{1}{2}\lambda}{n}=\frac{C-A}{n}$	$(n+\frac{3}{4})\frac{1}{2}\lambda=L$	Average λ meters
4	.71	28.20	30.12	1.92	29.31	15+	1.96	32.34	3.91
19	.80	27.83	29.92	2.09	29 12	14−	2.08	32.24	4.17
53	.90	27.59	29.81	2.22	28.91	13+	2.22	32.29	4.46
82	.99	27.29	29.67	2.38	28.68	12+	2.39	32.27	4.79
116	1.16	26.95	29.51	2.56	28.35	11	2.58	32.25	5.17
156	1.18	26.52	29.32	2.80	28.14	10+	2.81	32.32	5.62
							Av.	32.28	

Since the frequency of the oscillator is found to vary with the filament current it is better to calibrate a wave meter while taking these readings.

A very simple and efficient wave meter for short waves can be made by bending a piece of No. 12 bare copper wire into a circle about four inches in diameter and fastening to a wooden board. The ends of this circular wire should be about one inch apart. By means of a short screw at the center of the circle fasten a wire so as to slide over the

circular wire. Between the screw and one end of the circular wire insert a small fixed glass plate condenser. The capacity of this condenser should be about .0003 microfarads. Using photographic plate glass, the area of the two plates of sheet metal is about one square inch. The exact area must be found by trial. A dial or scale should be provided to measure the angular position of the slider.

The meter can be calibrated by setting the oscillator to a definite wave as measured on the Lecher wires and then removing the coupling loop and placing the wave meter in its place and by sliding the radial wire until resonance is indicated by the voltmeter in the plate circuit. With the Lecher wires of reasonable length, some five or six points can be thus obtained. When the angle or position of the radial wire is plotted against wave length it is found that a line is obtained which is nearly straight.

With this apparatus one has a very simple and exact method of obtaining frequencies of the order of one hundred thousand kilocycles.

INDIANA UNIVERSITY,
JUNE 4, 1925.

A SIMPLE CATHETOMETER

By H. H. Lowry

In many experiments it is desired to read differences in level over a fairly wide range to ± 0.1 mm. Direct estimation on a scale graduated in millimeters cannot be made to this degree of accuracy on account of the errors introduced by parallax. The telescopic cathetometer, on the other hand, reading to 0.01 mm, often has too small a range or is more troublesome to operate than the nature of the results justifies. For such

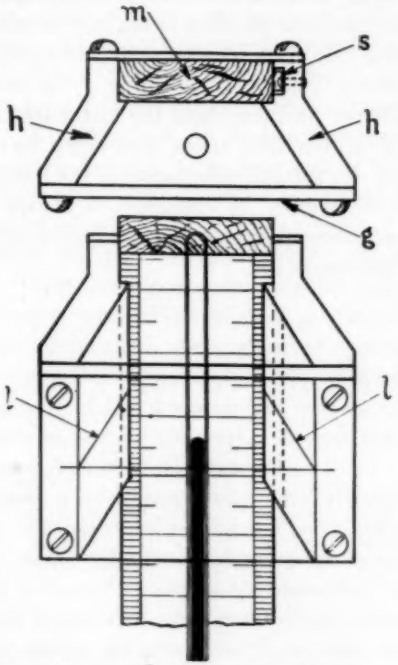

Fig. 1. *Diagrams of the cathetometer*

cases, I have found the instrument shown in the accompanying figure very convenient. In this figure the upper diagram shows the instrument in cross-section while the lower diagram shows it viewed at an angle from above. Essentially, this device consists of two brass holders, *h*, which slide on a meter stick, *m*, graduated in millimeters and which carry an ordinary slide rule glass, *g*. For convenience in assembly, the

holes in the glass, *g*, should be larger than the screws holding the glass in place in order to facilitate alignment of the etched line of the glass with the lines, *l*, on each of the holders which extend all the way to the surface of the stick. The instrument is then adjusted so that the lines, *l*, on the holders and the hair line of the glass, *g*, lie in a plane perpendicular to the plane of the surface of the meter stick. When so assembled it is possible at all times to see the lines, *l*, and the line of the slide-rule glass sharply projected on the scale of the meter stick. Then, by taking advantage of the distance of the glass from the meter stick, and moving the glass so that the hair line of the glass simultaneously crosses the surface of the mercury level to be read and covers the etched lines on both holders, the chance of parallax is entirely eliminated. The fine hair line on the slide rule glass allows one to read easily the position on the meter stick within ± 0.1 mm. A spring, *s*, on one of the holders secures the slide in any position along the meter stick.

The same principle described above may often be of advantage in other types of work. By suitable adaptation of the holders, for instance, an instrument could readily be designed to enable more accurate reading of burettes, thermometers, etc., than is generally accomplished.

BELL TELEPHONE LABORATORIES, INC.,
NEW YORK, N. Y.

A NEW SELF-REGISTERING SPECTROTHERMOGRAPH

By Joseph W. Ellis

In infrared spectroscopy use has usually been made of visual methods in observing the details of both emission and absorption spectra. Photographic plates have been sensitized and used in the study of the solar spectrum to 1μ,[1] and in the study of absorption spectra to a slightly greater wave length than this.[2] In his later work on solar radiation Langley[3] adopted a recording device for the registering of the sun's spectrum to 5.5μ. This device consisted of a strip of photographic paper, the vertical motion of which was co-ordinated with the rotation of the dispersing prism. The excursions of a spot of light reflected from the galvanometer upon this photographic paper traced the distribution of solar energy. A comparison of duplicate records shows that his device was exceedingly faithful in the registration of details.

The writer has previously described a self-registering infrared spectrograph[4] equipped with two flint glass prisms of medium density. The records were traced upon a strip of bromide paper fastened upon a revolving drum. With this mechanism the absorption spectra of some thirty organic liquids were obtained to 2.5μ. Numerous absorption bands, previously undetected, were observed, many of which were found to fit an approximate parabolic series characteristic of hydrocarbons.[5] The results of the investigation were so fruitful that it has been felt advisable to resume the work. To this end a new recording spectrothermograph has been constructed.

Fig. 1 shows both a horizontal and a vertical cross-sectional sketch of the apparatus. The source of radiation S is the concentrated filament of a street lamp, which may be replaced by an incandescent platinum strip whenever it is desired to escape the absorption of the glass of the lamp. The source is operated on direct current, since the fluctuations of an alternating voltage are great enough to mask many of the details being sought. The radiation is brought to a focus upon the symmetrical slit B by means of a quartz lens L of 10 cm focal length. The rays are reflected by means of the plane front surface mirror M upon a parabolic

[1] Abney, Phil. Trans., *171*, p. 653; 1880.
[2] Abney and Festing, Phil. Trans., *172;* 1881.
[3] Langley, Brit. Assoc. Rep., p. 465; 1894.
[4] Ellis, Phys. Rev., *23*, p. 48; 1924.
[5] Ellis, J.O.S.A. & R.S.I., *8*, p. 1, 1924.

mirror R of 3.4 cm aperture and 30.4 cm focal length; they then suffer dispersion as they pass through a 30° and a 60° quartz prism. The former prism is set so that the rays strike one face practically normally, while the second prism is fixed for minimum deviation for an approximate median wave length value. The plane mirror N causes the rays to retrace their paths through the prisms, causing a narrow spectral region to become focused upon the Hilger thermopile T, which actuates a Leeds and Northrup galvanometer, G. This galvanometer has a sensitivity of 9.3 mm per mv. Rotation of N causes the spectrum

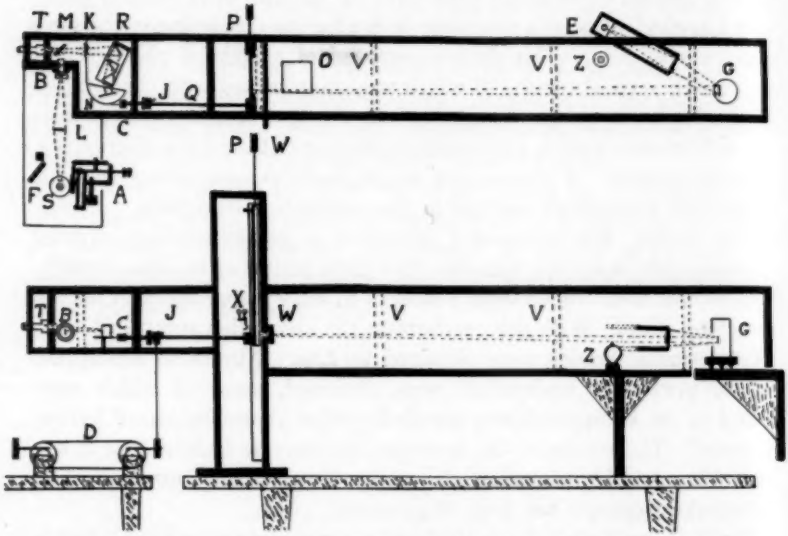

FIG. 1.—*Horizontal and vertical cross-sectional diagrams of the self-registering spectrothermograph.*

to pass continuously over the thermo-elements. This is accomplished by having the mirror mounted on a table capable of rotation about a vertical axis and held taut by a spring K. Uniform motion of the mirror table is secured by means of a threaded collar C on the shaft Q, which in turn is driven by a motor through two worm reduction gears D. At the other end of the shaft is a pair of small bevel gears which lower a plate holder by means of a rack and pinion. Uniform motion of the plate holder was not secured until it was counterbalanced by a weight over the pulley P.

The energy distribution curves are recorded upon regular photographic plates, 4.6″ by 17″, securely held in the holder. The tracing

system consists of a straight filament automobile lamp E, a small portion of whose image is allowed to fall upon the plate through a mm aperture running the whole width of the plate, when the shutter W is removed. It was found necessary to introduce diaphragms V to prevent a fogging of the plate due to stray light originating from E. O represents a window for the observation of the position of the tracing image at the beginning of an exposure.

The following steps will reveal the procedure followed in taking a record. The yellow sodium line is used as the reference line in the spectrum. This light is secured without the removal of the source S by swinging the mirror F around to throw the light from the arc A upon the initial slit. The line, observed through the eye-piece on the thermopile mount, is brought into approximate coincidence with the thermo-elements through a rotation of the shaft by hand. The plate-holder is then engaged and its cover removed. The pin J is inserted and the motor system caused to bring the sodium line into exact coincidence with the thermo-elements. At this time the shutter W is removed and the lamp Z turned on for a second to give a reference line exposure. About ten minutes are required to trace the spectrum to 3μ. At the completion of a run the motor is automatically shut off by a trip X which is released by a stop on the plate holder.

It is found possible to prevent fluctuations of the tracing beam due to jarring by mounting the galvanometer on an isolated support fastened to the wall, and by mounting the driving mechanism and the spectrograph on separate tables.

For investigations of the infrared region of the spectrum to 2.5μ by means of prism spectrographs, three substances are available for prism material: quartz, carbon bisulfide and flint glass. The former of these has been more generally used, although each of the other two has certain advantages. In Fig. 2 are shown the comparative dispersion curves of these three substances. Calculations for the glass were made from one sample of flint glass[4] only, the refractive indices of which were 1.653 and 1.612 for wave length values of 0.589μ and 2.7μ respectively. Curve A shows the ratio of the dispersive powers of this glass and quartz over the spectral region from 0.8μ to 2.7μ. For short wave lengths the glass has twice the dispersion of quartz; at about 1.5μ they have practically equal dispersions; while at 2.7μ the quartz has twice the dispersion of the glass. The ratio of the dispersive powers of CS_2

[4] Points for curve B were obtained from the dispersion curves for quartz and carbon bisulfide given in Scientific Papers of the Bureau of Standards, No. 401, p. 712.

and quartz changes even more radically, decreasing from a value of four to a value of one tenth, as shown by curve *B*.[6] Curve *C* shows the relative dispersions of the glass and CS_2, and was calculated from curve *A* and *B*. The three curves show that for a study of the limited region to 1.4μ best results can be obtained with carbon bisulfide prisms, although for use throughout the whole region to 2.5μ better results can be secured from flint glass. If the investigation is confined mainly to the region 1.5μ to 3μ quartz should be used.

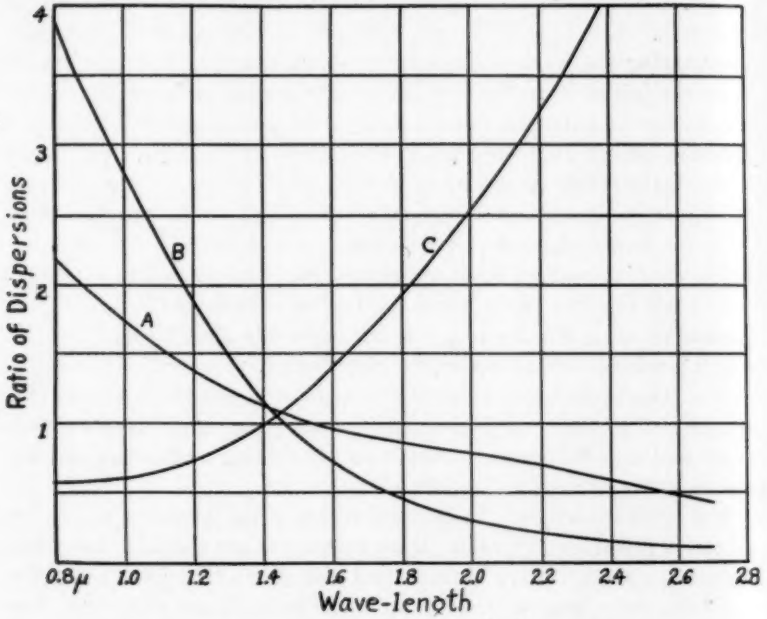

FIG. 2.—*Curve A*: *Ratio of dispersions of a flint glass and quartz.*
Curve B: *Ratio of dispersions of* CS_2 *and quartz.*
Curve C: *Ratio of dispersions of the flint glass and* CS_2.

Fig. 3*a* shows the energy distribution curve produced by the former recording spectrothermograph equipped with flint glass prisms,[7] the total refracting angle of which was equivalent to 120°. Fig. 3*b* shows a similar energy curve produced with the present self-registering machine equipped with quartz prisms, with a total refracting angle equivalent to 180°. The former shows the considerably greater dispersion of the

[7] Phys. Rev., *23*, p. 56; 1924.

shorter wave lengths. The rather abrupt decline of the curve beyond 1.5μ is due to the decreasing dispersion and the increasing general absorption by the glass. The latter shows the crowding together of the shorter wave lengths and increasingly better dispersion beyond 1.5μ.

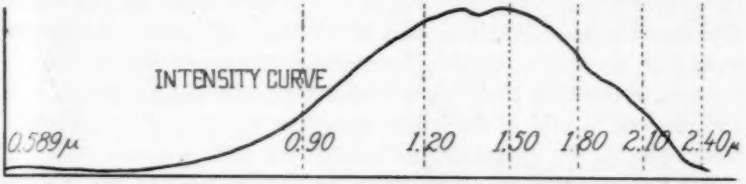

FIG. 3a.—*Energy distribution from an incandescent solid as produced by flint glass prisms*

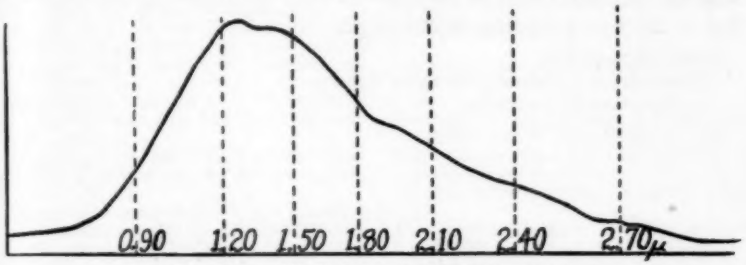

FIG. 3b.—*Energy distribution as produced by quartz prisms.*

Fig. 4 shows the absorption spectrum in the region 2μ to 3μ produced by a 0.5 mm cell of toluene. The intensity of the source was much greater than that used in the record of 3*b*. The dotted line has been inserted to represent the initial distribution of energy.

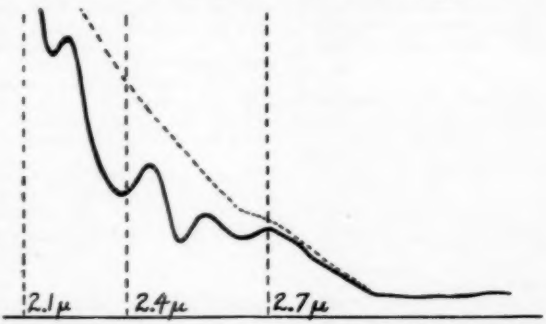

FIG. 4.—*Absorption spectrum between 2μ and 3μ of a 0.5 mm cell of toluene.*

Practically all substances which are transparent to the visible rays have regions of selective absorption in the near infrared. In numerous

instances these bands of absorption have been shown to constitute approximately linear series, whose members, gradually becoming weaker, become more and more closely spaced in the shorter wave length region. The purpose of this resumed investigation is to subject the limited region between 2μ and 3μ to a greater dispersion and resolution than has heretofore been used in this work, to further separate the numerous absorption bands characteristic of organic liquids, and to attempt to establish their origin within the absorbing molecule. It is also planned to subject the longer wave length region to an investigation, replacing the quartz prisms by rock salt prisms.

The writer wishes to acknowledge his indebtedness to Mr. Leo P. Delsasso and Mr. Lewis A. Delsasso for their assistance in the construction of the new recording spectrograph.

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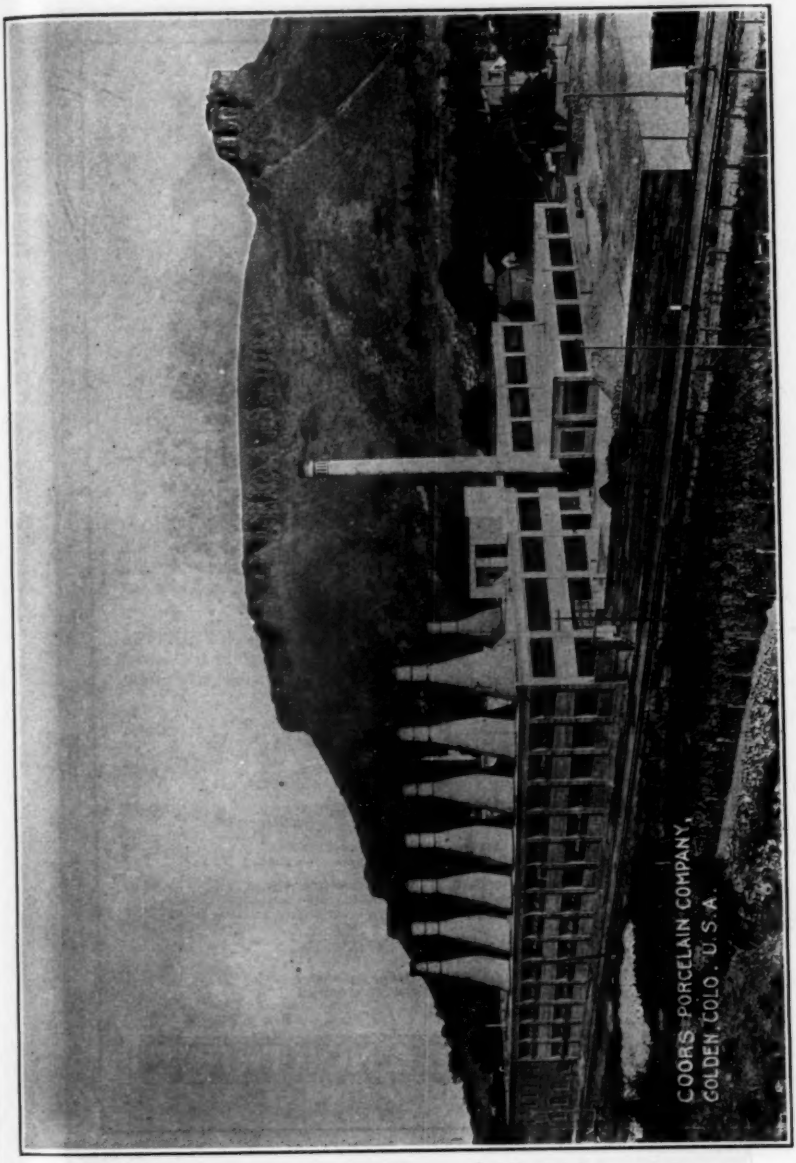
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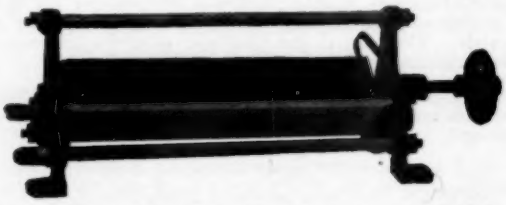

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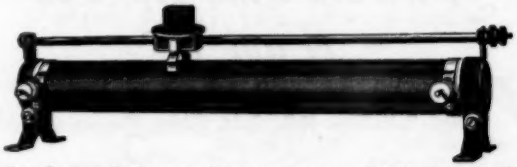

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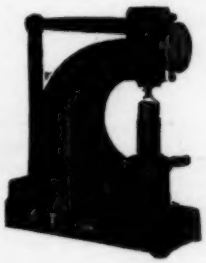

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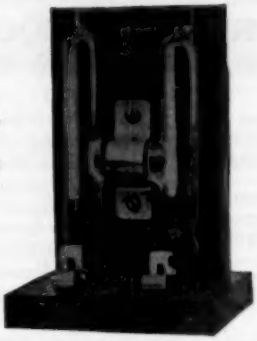

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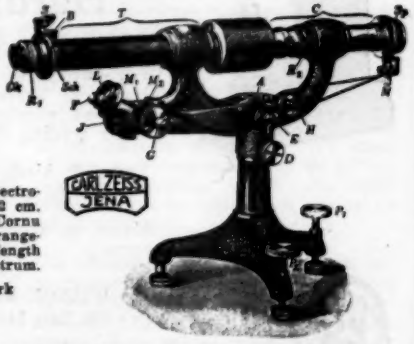

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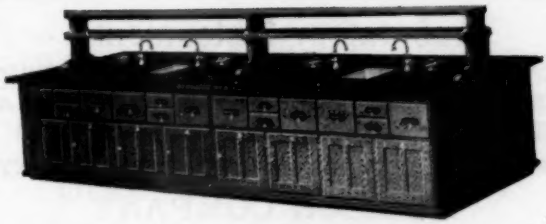

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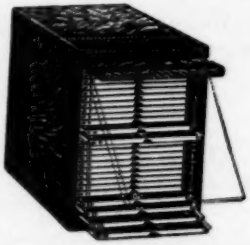

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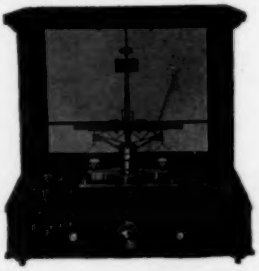

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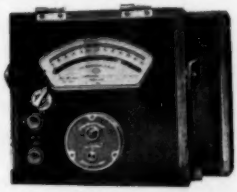

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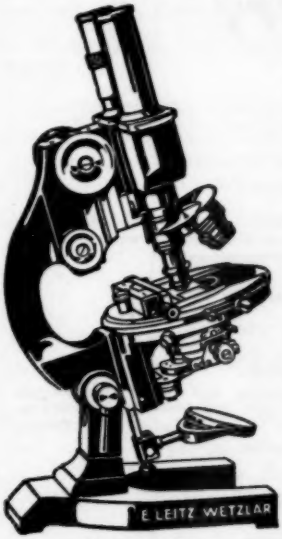

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